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Adsorption of Methylamine on Amorphous Ice under Interstellar Conditions. A Grand Canonical Monte Carlo Simulation Study

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3 **Adsorption of Methylamine on Amorphous Ice under Interstellar**
4 **Conditions. A Grand Canonical Monte Carlo Simulation Study**
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48 **Running title:** Adsorption of methylamine on ice
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Abstract:

The adsorption of methylamine at the surface of amorphous ice is studied at various temperatures, ranging from 20 K to 200 K, by grand canonical Monte Carlo simulations under conditions that are characteristic to the interstellar medium (ISM). The results are also compared with those obtained earlier on crystalline (I_h) ice. We found that methylamine has a strong ability of being adsorbed on amorphous ice, involving also multilayer adsorption. The decrease of the temperature leads to a substantial increase of this adsorption ability, thus, considerable adsorption is seen at 20-50 K even at bulk gas phase concentrations that are comparable with that of the ISM. Further, methylamine molecules can also be dissolved in the bulk amorphous ice phase. Both the adsorption capacity of amorphous ice and the strength of the adsorption on it are found to be clearly larger than those corresponding to crystalline (I_h) ice, due to the molecular scale roughness of the amorphous ice surface as well as to the lack of clear orientational preferences of the water molecules at this surface. Thus, the surface density of the saturated adsorption monolayer is estimated to be $12.6 \pm 0.4 \mu\text{mol}/\text{m}^2$, 20% larger than the value of $10.35 \mu\text{mol}/\text{m}^2$, obtained earlier for I_h ice, and at low enough surface coverages the adsorbed methylamine molecules are found to easily form up to three hydrogen bonds with the surface water molecules. The estimated heat of adsorption at infinitely low surface coverage is calculated to be $-69 \pm 5 \text{ kJ}/\text{mol}$, being rather close to the estimated heat of solvation in the bulk amorphous ice phase of $-74 \pm 7 \text{ kJ}/\text{mol}$, indicating that there are at least a few positions at the surface where the adsorbed methylamine molecules experience a bulk-like local environment.

1. Introduction

The origin and formation of amino acids are of particular interest in astrochemical research, because their presence in the interstellar medium (ISM) may provide clues to the delivery of prebiotic molecules to the early Earth, the possible origins of life on Earth,¹⁻³ and the possibility of Earth-like life elsewhere in the Universe.⁴ Glycine and methylamine (CH_3NH_2) are not just simple structural analogs (related to each other by the presence or absence of the carboxyl group), but methylamine is also proposed to be a precursor of glycine. In the interstellar medium, CH_3NH_2 can be formed either by CH_4 and NH_3 , well known to be abundant in the ISM, under cosmic ray irradiation,^{5,6} or by the hydrogenation reaction of HCN on icy dust surfaces. CH_3NH_2 molecules that are trapped at solid surfaces can then thermally react with CO_2 to form carbamate, which can be converted to a glycine salt under vacuum ultraviolet irradiation.⁷ Alternative pathways of this reaction, occurring through the CH_2NH_2 radical^{8,9} or acetic acid¹⁰ were also proposed in the literature.

Both glycine and methylamine compounds are common in the terrestrial biosphere,¹ and both have also been detected in comet-exposed material from the *Stardust* sample return mission to comet Wild 2,¹¹ by the Cometary Sampling and Composition (COSAC) instrument onboard the *Rosetta Philae* mission,¹² as well as in multiple extraterrestrial samples, including carbonaceous chondrites.¹³⁻¹⁵ Carbonaceous chondrites, notably the CI (e.g. Orgueil) and CM (e.g. Murchinson) groups, contain high percentages (3% to 22%) of water,¹⁶ and also methylamine in the concentration of 331 nmol/g (Orgueil) and 85 nmol/g (Murchison).¹⁷ Generally, interstellar¹⁸ and cometary¹⁹ dust grains are frequently covered by amorphous solid water, this mantle also traps volatile reactants, and the water molecule can act both as a catalyst and as a chemical reactant.²⁰ In order to characterize methylamine astrochemistry, Vinogradoff et al. reported a laboratory experiment, in which methylamine and formaldehyde were found to quickly react at interstellar or cometary ice analogues at astronomically relevant temperatures with a measured activation energy of 1.1 ± 0.05 kJ/mol.²¹ However, in the absence of relevant experiments, desorption behavior of methylamine from the ice surface was estimated to be identical with that of ammonia (with a value of 3×10^{12} s as the pre-exponential factor, and 25 kJ/mol as the activation energy).²¹ As this example also shows, a major stumbling-block in our understanding of prebiotic chemistry in the ISM is the lack of a standardized and comprehensive approach to simulate grain-surface chemistry.²² Furthermore, improved gas-

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3 grain astrochemical models need to be developed in order to interpret the high-resolution data
4 provided by Atacama Large Millimeter Array (ALMA).
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7 Besides laboratory experiments, molecular details of the adsorption of methylamine at
8 icy surfaces can also be investigated by computer simulation methods, in order to improve the
9 current adsorption models used in astrochemistry. Such methods can well complement
10 experiments, as they can provide a full, three-dimensional insight of atomistic resolution into
11 the system of interest.²³ Among the various computer simulation techniques, the grand
12 canonical Monte Carlo (GCMC) method^{23,24} is particularly suitable for studying adsorption,
13 since here the chemical potential rather than the number of the adsorbate molecules in the basic
14 box is fixed, and thus, by systematically varying the chemical potential and determining the
15 number of adsorbate molecules in a set of simulations, the adsorption isotherm can be
16 determined, and simulation results can be analyzed in detail at surface coverage values that are
17 relevant for the given adsorption process. The GCMC method has been successfully applied in
18 the past two decades for a set of systems, such as for the adsorption of various small molecules
19 at carbonaceous surfaces,²⁵⁻³¹ metal oxides,³²⁻³⁵ covalent organic frameworks,³⁶⁻³⁸ crystalline
20 ice,³⁹⁻⁴⁸ water clathrates,⁴⁹ kaolinite,^{50,51} zeolites,⁵²⁻⁵⁸ self-assembled monolayers,^{59,60} and
21 protein crystals.⁶¹
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32 Since icy surfaces in the interstellar medium are predominantly covered by low density
33 amorphous ice (LDA),^{18,19} here we study the adsorption of methylamine at the surface of LDA
34 ice by GCMC simulations at temperatures that are relevant to the interstellar medium (i.e., a
35 few tens of K). Besides its potential role in prebiotic evolution, methylamine, released
36 primarily by decaying bodies,⁶² is also an abundant atmospheric pollutant, being involved in
37 the catalytic ozone destruction process occurring at the polar stratospheres⁶³ as well as
38 increasing aerosol nucleation rates in the lower troposphere.⁶⁴ For this purpose, recently we
39 performed a detailed GCMC analysis of the adsorption of methylamine at the surface of
40 crystalline, I_h ice at the tropospheric temperature of 200 K. Thus, the present study provides
41 also an excellent opportunity to investigate in detail the role of the state of the adsorbing phase
42 (i.e., crystalline vs. amorphous ice) as well as that of the temperature in the details of the
43 adsorption process. For this purpose, here we determine the adsorption isotherm of
44 methylamine at the surface of LDA ice, and analyze in detail the properties of the adsorption
45 layer at the temperatures of 200 K, 150 K, 100 K, 50 K, and 20 K, corresponding to the
46 adsorption in the colder parts of the interstellar medium. Further, the comparison of the results
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3 obtained at 200 K with our earlier data obtained at the surface of I_h ice⁴⁷ provides information
4 on how the properties of the adsorption layer depends on the structure of the adsorbing phase,
5 whereas the comparison of the results obtained at different temperatures can shed light on the
6 temperature dependence of the adsorption process, and even allows us to extrapolate to lower
7 temperatures, at which computer simulation studies cannot be done within reasonable time.
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11 The paper is organized as follows. In sec. 2 details of the performed calculations,
12 including GCMC simulations and ITIM analysis, are given. The results concerning the
13 adsorption isotherm, the building up of the subsequent molecular layers of the adsorbate as
14 well as the orientation and energetics of the adsorbed methylamine molecules that are in direct
15 contact with the ice phase are discussed in detail in sec. 3. Finally, in sec. 4 the main
16 conclusions of this study are summarized.
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24 **2. Computational Details**

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27 **2.1. Grand Canonical Monte Carlo Simulations.** The adsorption of methylamine at
28 the surface of low density amorphous ice has been simulated, using the Monte Carlo method,
29 on the grand canonical (μ, V, T) ensemble at the temperatures (T) of 200 K, 150 K, 100 K, 50 K,
30 and 20 K. The X , Y , and Z edges of the rectangular basic simulation box have been 100 Å,
31 35.926 Å, and 38.891 Å, respectively, X being the axis perpendicular to the ice surface. The
32 basic box has consisted of 2880 water molecules. At each temperature, simulations have been
33 performed at several chemical potentials of methylamine, ranging from values corresponding
34 to practically no methylamine molecules in the basic box to those corresponding to the
35 condensed phase of methylamine. The chemical potential values at which the simulations have
36 been performed at the various temperatures, as well as the mean number of the methylamine
37 molecules present in the basic box, resulted from these simulations, are summarized in Tables
38 S1-S5 of the supporting information.
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48 To be consistent with our previous study concerning I_h ice,⁴⁷ water and methylamine
49 molecules have been described by the TIP5P model⁶⁵ and the potential model proposed by
50 Impey et al.,⁶⁶ respectively. TIP5P is known to be one of the best water models in describing
51 low temperature aqueous phases,⁶⁷ as it reproduce very well, among others, the temperature of
52 maximum density^{65,67} as well as the melting point⁶⁷ of water. Further, TIP5P reproduces the
53 LDA/HDA liquid-liquid phase transition of water in the temperature range considered here.⁶⁸
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3 Both of these models used are rigid and pairwise additive, i.e., the total potential energy of the
4 system is assumed to be the sum of the contributions of all molecule pairs. The interaction
5 energy of a molecule pair consists of the Lennard-Jones and charge-charge Coulomb
6 contributions of all the respective pairs of interaction sites. The CH₃ group of the methylamine
7 molecule is treated as a single interaction site (united atom), whereas the water model has two
8 non-atomic interaction sites, marked by L, located at the positions of the two lone pairs of the
9 O atom. The interaction of a molecule pair is truncated to zero beyond the center-center cut-off
10 distance of 12.5 Å. The interaction and geometry parameters of the potential models used are
11 collected in Tables 2 and 3 of Ref. 47, respectively.
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19 The simulations have been performed using the program MMC⁶⁹ in the same way as
20 described in our earlier paper.⁴⁷ Thus, in every Monte Carlo step either, by 50% probability, a
21 randomly chosen molecule has been randomly translated by no more than 0.25 Å and randomly
22 rotated by no more than 15°, or by 50% probability, the number of the methylamine molecules
23 in the basic box has been attempted to be changed by inserting or removing a molecule. Water
24 and methylamine molecules have been selected for particle displacement steps with equal
25 probabilities, and methylamine insertions and deletions have also been performed with 50%-
26 50% probabilities. The insertion/deletion attempts have been made using the cavity biased
27 scheme of Mezei,^{70,71} thus, insertions have only been attempted into centers of empty cavities
28 of the radius of at least 2.6 Å. Suitable cavities have been searched for along a 100×100×100
29 grid, which has been regenerated after every 10⁶ Monte Carlo steps. Particle displacement and
30 insertion/deletion attempts have been accepted or rejected according to the standard Metropolis
31 algorithm,^{23,72} and according to the acceptance criterion of the cavity biased scheme,^{70,71}
32 respectively.
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43 To create the LDA ice phase and surface, we started from the crystalline I_h ice phase
44 used in our previous work. This phase was melted by thermalizing it, on the canonical (N, V, T)
45 ensemble, at 350 K by performing 3×10⁸ Monte Carlo steps, followed by another 10⁸ Monte
46 Carlo steps at 300 K. The melted system was then quenched by setting the temperature to
47 200 K, and performing another 10⁸ Monte Carlo steps. Then two methylamine molecules were
48 added to the vapor phase of the system, and this configuration has been used as the starting
49 point of all grand canonical ensemble simulations. The system has then been equilibrated at
50 every temperature and chemical potential by performing 10⁹ – 3×10⁹ Monte Carlo steps, until
51 neither the average total energy of the system nor the mean number of methylamine molecules
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3 have shown even traces of a systematic drift. The mean number of the methylamine molecules
4 has then been determined in every case by generating a 2×10^8 Monte Carlo steps long
5 equilibrium trajectory. Equilibrium snapshots of the 20 K system are shown in Figure 1, both
6 in top and side views, as obtained at four different chemical potential values of methylamine.
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10 To investigate the properties of the adsorption layer in detail, at selected chemical
11 potential values, 5000 equilibrium sample configurations, separated by 4×10^5 Monte Carlo
12 steps long runs each, have been saved from the 2×10^9 Monte Carlo steps long production runs
13 for further evaluation. At each temperature four such chemical potential values have been
14 chosen. The first of these values always corresponds to the presence of only very few, isolated
15 methylamine molecules at the ice surface, the second one to a partly unsaturated monolayer, in
16 which the methylamine molecules are no longer isolated from each other, the third one to a
17 more or less saturated monolayer, while the fourth one to multilayer adsorption. For
18 comparison with our earlier results, at 200 K dumping of configurations has also been done at
19 two more chemical potential values, at which detailed analysis of the adsorption layer on I_h ice
20 was earlier performed.⁴⁷ Finally, for reference purposes, configurations have also been saved
21 for analyses at a μ value corresponding to the condensed phase of methylamine at 200 K.
22 These μ values, together with the mean number of methylamine molecules resulted from the
23 corresponding simulations, are collected in Table 1, and are also indicated in Tables S1-S5 of
24 the supporting information.
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38 **2.2. Identification of the Dissolved and First Layer Methylamine Molecules.** It has
39 turned out from the simulations that, unlike in the case of crystalline I_h ice, methylamine
40 molecules are not only adsorbed at the surface of the amorphous LDA ice, but they are also
41 incorporated in the bulk ice phase, as seen also in some of the snapshots of Fig. 1. This finding
42 is in a clear accordance with the results of the experiments of Vinogradoff et al., performed on
43 methylamine/water mixtures under astrochemical conditions.²¹ Further, the surface of the
44 amorphous ice phase, unlike that of the crystalline ice phase used in our previous simulation,⁴⁷
45 is corrugated on the molecular length scale. Therefore, the first molecular layer of the adsorbed
46 phase of methylamine (i.e., the methylamine molecules that are in a direct contact with the ice
47 phase) cannot simply be identified in the conventional way, with the first peak of the
48 methylamine density profile. Instead, first layer methylamine molecules have to be identified
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3 with an intrinsic surface analyzing method.⁷³ Further, the methylamine molecules forming the
4 first layer are needed to be distinguished not only from those belonging to one of the
5 subsequent molecular layers in the adsorbed phase, but also from the ones that are dissolved
6 into the bulk amorphous ice phase.
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10 To perform the identification of the methylamine molecules forming the first adsorbed
11 molecular layer as well as those inserted into the amorphous ice phase, we have applied a
12 modified version of the Identification of Truly Interfacial Molecules (ITIM) method,
13 developed originally to identify the instantaneous surface of fluid phases in computer
14 simulations.⁷⁴ This complex goal has been achieved in two major steps. In the first one, the
15 ITIM algorithm has been performed solely on the ice phase, to identify the molecularly
16 corrugated boundaries of the adsorbent. As a result, every methylamine molecule residing
17 between these boundaries can be considered as being dissolved in the ice phase, and hence can
18 be excluded from further analyses. This first round of the ITIM analysis has been followed by a
19 second one, this time performed “inside-out” on the remaining methylamine molecules, to
20 identify the innermost adsorbates in the immediate vicinity of the ice surface. This set of
21 interface methylamine molecules has been considered as the first adsorbed layer in all
22 subsequent analyses. In the ITIM procedure, probe spheres of a radius of 2 Å have been moved
23 perpendicular to the plane of the macroscopic interface until they “touched” the outmost atom
24 of the phase to be analyzed. Probes were “launched” from a grid set up above the surface. The
25 spacing of the grid was set to 0.5 Å. The choice of these parameters was previously found to
26 ensure an optimal sampling for molecularly corrugated surfaces.^{73,74} This method is illustrated
27 in Fig. 1, where methylamine molecules belonging to the first molecular layer of the adsorbed
28 phase are shown by yellow, those being in the outer part of the adsorption layer by cyan, while
29 those inserted into the ice phase by dark blue color.
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46 **3. Results and Discussion**

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49 **3.1. Adsorption Isotherm and Density Profiles.** The average number of methylamine
50 molecules present in the basic simulation box, $\langle N \rangle$, is shown as a function of the chemical
51 potential in Figure 2 as obtained from our GCMC simulations at the five temperatures
52 considered. The chemical potential values at which sample configurations have been saved for
53 detailed analyses are also indicated in the figure. It should be noted that the value of $\langle N \rangle$ has
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3 been calculated on-the-fly, whereas, due to its computational cost, the ITIM procedure
4 described in sec. 2 can only be performed, and hence also the distinction between the adsorbed
5 and dissolved methylamine molecules can only be made on saved sample configurations.
6 Therefore, the isotherms shown in Fig. 2 include both the adsorbed and dissolved methylamine
7 molecules. The isotherms corresponding to different temperatures are rather similar to each
8 other in shape: they all rise sharply and continuously up to the sudden jump corresponding to
9 the point of condensation, without exhibiting any marked plateau. The very steep rise of the
10 isotherms, occurring immediately before condensation, suggests that the adsorption of
11 methylamine is not limited to one single molecular layer. As expected, the isotherms are
12 shifted to higher chemical potential values with decreasing temperature. The μ values
13 corresponding to the point of condensation, denoted here as μ_0 , are estimated from the position
14 of the steepest rising part of the isotherms to be -26.26, -27.76, -30.20, -32.34, and
15 -33.66 kJ/mol at 20, 50, 100, 150, and 200 K, respectively. As is seen from Figure 3, the value
16 of μ_0 increases practically linearly with decreasing temperature. Considering that, for one
17 component, μ is simply the molar free energy, and hence the molar entropy, S^m , is related to its
18 temperature derivative as $S^m = -(\partial\mu/\partial T)$, the observed linear temperature dependence of μ_0
19 implies that the corresponding molar entropy is constant (i.e., 41.9 ± 2.7 J/mol K).

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33 The comparison of the isotherms obtained at 200 K at the surfaces of crystalline, I_h ⁴⁷
34 and amorphous ice is shown in the inset of Fig. 2. As is seen, there are several important
35 differences between the two isotherms. First, at low μ values, i.e., below about -40 kJ/mol, the
36 isotherm corresponding to amorphous ice goes consistently above that of the I_h ice. Since in
37 this chemical potential range even the first molecular layer of methylamine is far from being
38 saturated, this difference indicates stronger interaction of the methylamine molecules with the
39 corrugated surface of amorphous ice, containing several troughs on the molecular length scale
40 within which an adsorbed molecule can have more contact with the surrounding waters, than
41 with the flat surface of I_h ice. Second, the clear plateau of the isotherm corresponding to I_h ice
42 in the μ range between about -40 and -35 kJ/mol, corresponding to the saturated monolayer, is
43 completely missing in the case of amorphous ice. Instead, this latter isotherm rises
44 continuously even in this μ range, indicating the building up of outer molecular layers of
45 methylamine here. The lack of particular stability of the saturated monolayer at the amorphous
46 ice surface is probably due to the fact that the adsorbed monolayer reflects the corrugation of
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3 the ice surface, and hence it also has several pockets of negative local curvature, in which the
4 building up of the second molecular layer can start earlier than on a relatively flat monolayer,
5 present at the surface of I_h ice. Finally, above the point of condensation the isotherm
6 corresponding to amorphous ice goes again above that of I_h ice. However, in this μ range this
7 difference simply reflects the higher density of the somewhat disordered amorphous ice than
8 that of the I_h ice, which leaves more space for the methylamine molecules in the basic
9 simulation box.

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15 It should be emphasized, however, that the isotherm obtained at amorphous ice contains
16 also the methylamine molecules that are dissolved in the ice phase, while no such dissolved
17 molecules were found in the case of I_h ice.⁴⁷ Hence, all the observed differences of the two
18 isotherms in all the three above discussed ranges of μ can, at least partly, be accounted for
19 simply by the methylamine molecules dissolved in the bulk amorphous phase.

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24 We have also converted the obtained $\langle N \rangle$ vs. μ isotherms to the more conventional Γ
25 vs. p_{rel} form, where Γ is the surface density of methylamine, calculated simply as

$$\Gamma = \frac{\langle N \rangle}{2YZ}, \quad (1)$$

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32 and p_{rel} is the relative pressure, i.e., the ratio of the pressure of the system, p , and the pressure
33 corresponding to the point of condensation of methylamine at the given temperature, p_0 . p_{rel}
34 can be calculated using the value of μ_0 as³⁴

$$p_{\text{rel}} = \frac{p}{p_0} = \frac{\exp(\mu / k_B T)}{\exp(\mu_0 / k_B T)}, \quad (2)$$

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43 where k_B is the Boltzmann constant. It should be noted that since p_0 is the pressure of the
44 saturated vapor of methylamine, isotherms can only be converted to the $\Gamma(p_{\text{rel}})$ form up to the
45 point of condensation, i.e., when methylamine is still in its vapor phase.

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The obtained isotherms are shown in the Γ vs. p_{rel} form in Figure 4 as obtained at the
five temperatures considered; the corresponding values are also included in Tables S1-S5 of
the supporting information. It should be emphasized again that these isotherms still contain the
molecules that are dissolved in the bulk amorphous ice phase. As is seen, at a given p_{rel} value
the amount of adsorbed methylamine increases with decreasing temperature, and hence at

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3 lower temperatures multilayer adsorption occurs at lower p_{rel} values. It is also evident that the
4 low pressure rising part of the isotherm becomes progressively steeper as the temperature
5 decreases, due to the explicit dependence of p_{rel} on the temperature (see eq. 2). This steep rise
6 of the $\Gamma(p_{\text{rel}})$ isotherm at low temperatures results in considerable surface densities of
7 methylamine already around the relative pressure value of 10^{-30} at 20 K and 10^{-20} at 50 K. To
8 estimate the corresponding absolute pressure range, one needs the value of p_0 at these
9 temperatures, the value of which is clearly inaccessible from the simulations. The temperature
10 dependence of the experimental value of p_0 is described by the Antoine equation:⁷⁵

$$\ln p_0 = A - \frac{B}{T + C}, \quad (3)$$

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12 (p_0 and T being in units of Pa and K, respectively), with the Antoine parameter values of
13 $A = 21.92$, $B = 2383.1$ K, and $C = -37.574$ K, at least in the temperature range between 190 and
14 267 K.^{76,77} On the other hand, upon going to lower temperatures, eq. 3 is expected to provide
15 progressively worse estimate of p_0 , this estimate being 1.4×10^3 Pa at 200 K, 2 Pa at 150 K, and
16 about 10^{-7} Pa at 100 K. Using the very conservative estimate of 1 Pa for p_0 both at 20 K and
17 50 K, the gas phase concentration of methylamine corresponding to the above relative pressure
18 values (i.e., 10^{-30} at 20 K and 10^{-20} at 50 K) can be estimated through $c = p/RT$ as about
19 10^{-35} mol/dm³ (20 K) and 5×10^{-25} mol/dm³ (50 K), respectively. Considering that the typical
20 molecular number density of methylamine in the ISM is about in the order of
21 10^{-2} molecule/dm³, i.e., 10^{-26} mol/dm³,⁷⁸ our results reveal that considerable adsorption of
22 methylamine at icy surfaces can be expected at the density and temperature characteristic of
23 the cold part of the ISM.

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25 The $\Gamma(p_{\text{rel}})$ isotherms obtained at 200 K at the surfaces of I_h and amorphous ice are
26 compared in the inset of Fig. 4. This comparison corroborates the conclusion drawn from the
27 comparison of the $\langle N \rangle$ vs. μ isotherms that the saturated monolayer of methylamine consists
28 of more molecules at the surface of amorphous than at I_h ice.

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30 To better understand the nature of the adsorption, we have fitted the Langmuir
31 isotherm:^{79,80}

$$\Gamma = \Gamma_{\text{max}} \frac{p_{\text{rel}} K}{1 + p_{\text{rel}} K} \quad (4)$$

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3 to the obtained Γ vs. p_{rel} data at 200 K, 150 K, and 100 K. In eq. 4, the Langmuir parameters
4 Γ_{max} and K are the surface density of the saturated monolayer, and the Langmuir partition
5 coefficient, measuring the affinity of the adsorbate to the surface, respectively.^{79,80} The
6 Langmuir curves fitted to the simulated data points are indicated by dashed lines in Fig. 4. As
7 is seen, the obtained data can be reasonably well fitted up to a certain relative pressure value.
8 This fit is never perfect, since the relatively strong lateral interaction acting between the
9 adsorbed methylamine molecules introduces some slight deviation of the adsorption isotherms
10 from the Langmuir form, as it was already noted in our previous study concerning I_h ice.⁴⁷
11 Nevertheless, the fitted curve does not deviate strongly from the data points up to the p_{rel} value
12 of about 0.2, 0.05, and 0.02 at 200 K, 150 K, and 100 K, respectively, and this agreement also
13 involves the beginning of the plateau part in every case. It should be emphasized, however,
14 that, apart from the two points above $p_{\text{rel}} = 0.8$ at 200 K, all data points have always been
15 involved in the fitting procedure, not only the ones being in the p_{rel} range of reasonably good
16 fit. Clearly, at 200 K and 150 K the last two, while at 100 K the last three points that are used
17 in the fitting procedure correspond to much larger Γ values than what is predicted from the fit,
18 in spite of the fact that these points at intermediate p_{rel} values seemingly form a plateau of the
19 isotherm. This plateau clearly could not be fitted in any case. Instead, the fitted functions, and
20 thus also the values of the Γ_{max} parameter are determined predominantly by the low p_{rel} data
21 points, where the assumptions underlying the Langmuir isotherm are well satisfied. This fact
22 suggests that the difference between the plateau value of the data points and that of the fitted
23 Langmuir isotherm reflects primarily the effect of the methylamine molecules dissolved in the
24 bulk amorphous ice phase (and, possibly, also partly the effect of the molecules that are located
25 at the negative local curvature troughs of the saturated first molecular layer, forming already
26 traces of the second molecular layer). The Γ_{max} values obtained from the Langmuir fit resulted
27 in 12.4, 12.2, and 13.0 $\mu\text{mol}/\text{m}^2$ at 200 K, 150 K, and 100 K, respectively, suggesting that the
28 surface density of the saturated monolayer of methylamine at the surface of amorphous ice is
29 $12.6 \pm 0.4 \mu\text{mol}/\text{m}^2$. This value is considerably higher than that corresponding to the surface of
30 I_h ice of $10.35 \mu\text{mol}/\text{m}^2$,⁴⁷ reflecting the fact that the corrugated surface of amorphous ice can
31 host more adsorbed molecules in the first monolayer than the flat surface of I_h ice (This
32 difference is also seen from the Langmuir functions fitted to the two 200 K data sets in the
33 inset of Fig. 4.).
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To check whether our above approach is correct, we have calculated the mass density profile of all methylamine molecules as well as of only those forming the first molecular layer at selected chemical potential values, using the saved sample configurations, at the five temperatures considered. The obtained profiles are shown in Figure 5. As is seen, at least at the highest chemical potential value considered at every temperature, the two profiles are markedly different from each other, indicating that at these state points the adsorption extends well beyond the first molecular layer. Assuming that the first molecular layer is already saturated in these cases, the number of molecules forming this layer can be estimated. Further, this assumption can be confirmed considering the case of condensed methylamine at 200 K (see the upper panel of Fig. 5), where this layer must be saturated. The number of methylamine molecules belonging to this saturated first molecular layer turns out to be 210 ± 20 in every case, which corresponds to the Γ value of $12.5 \pm 1 \mu\text{mol}/\text{m}^2$, being in excellent agreement with the value estimated from the Langmuir fit of $12.6 \pm 0.4 \mu\text{mol}/\text{m}^2$. The Γ values corresponding to the first molecular layer of methylamine at the selected chemical potential values, Γ^{first} , along with the corresponding p_{rel} values, are also included in Table 1.

Having the adsorbed and dissolved methylamine molecules distinguished from each other, at least at the chemical potential values at which sample configurations have been collected, the dissolution (solubility) isotherms can also be, at least, estimated. The average number of the dissolved methylamine molecules, $\langle N_{\text{sol}} \rangle$, is shown as a function of the chemical potential at the five temperatures considered in Figure 6, while the inset of the figure shows these data in the c vs. p_{rel} form, where c is the bulk ice phase concentration of methylamine:

$$c = \frac{\langle N_{\text{sol}} \rangle}{X_{\text{ice}}YZ}, \quad (5)$$

where the value of X_{ice} , i.e., the X range of extension of the amorphous ice phase, has been estimated to be 60 \AA from the density profile of the water molecules (see Fig. 5). The c values obtained at different chemical potentials and temperatures are also included in Table 1. In interpreting the $c(p_{\text{rel}})$ solubility isotherms it should be recalled that, by performing particle insertion and deletion steps, the GCMC method efficiently removes any barrier corresponding to the direct transport of the molecules between markedly different environments (e.g., the bulk

vapor phase, ice surface, and bulk ice phase), and simply results in configurations corresponding to the thermodynamic equilibrium. Therefore, our results show that in thermodynamic equilibrium a non-negligible amount of methylamine molecules are dissolved in the bulk LDA phase, but cannot say anything about the possible kinetic hindrance of reaching this equilibrium situation.

3.2. Orientation of the First Layer Methylamine Molecules. The full description of the relative orientation of a rigid body relative to an external direction requires the use of two independent orientational variables, such as the two polar angles of the external vector in a suitably chosen coordinate frame fixed to the rigid body. Therefore, the orientational statistics of such rigid bodies, such as rigid molecules in a computer simulation, relative to an external direction can only be fully described by the bivariate joint distribution of these variables.^{81,82} In analyzing the orientational preferences of the first layer methylamine molecules relative to the ice surface (or, equivalently, to the surface normal), we have chosen these variables in the following way. The frame is fixed to the individual methylamine molecules; its origin is the N atom, axis z points along the N-CH₃ bond from the N atom to the CH₃ group, axis y is parallel with the segment that joins the two hydrogen atoms of the NH₂ group, while axis x is perpendicular to the above two axes, and it is oriented in such a way that the x coordinates of the amine H atoms are positive. The orientational variables ϑ and ϕ are then the polar angles of the surface normal axis, \underline{X} , pointing, by our convention, away from the ice phase (see Figure 7). To analyze the orientation of the surface water molecules, we have defined the local frame, fixed to the individual water molecules, in such a way that its origin is the O atom, axis x is the molecule normal, axis y is parallel with the line connecting the two H atoms, and axis z points along the bisector of the H-O-H angle, while ϑ and ϕ are again the polar angles of \underline{X} in this frame (see Fig. 7). Due to the symmetry of the methylamine and water molecules, the above frames are always chosen such that the inequalities $\phi \leq 180^\circ$, and $\phi \leq 90^\circ$, respectively are also satisfied. It should also be noted that while ϑ is the angle between two spatial vectors, ϕ is that of two planar ones (i.e., two vectors that both lay, by definition, in the xy plane of the local frame), and hence random surface orientation results in a uniform bivariate distribution only if $\cos\vartheta$ and ϕ are chosen to be the orientational variables.^{81,82}

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3 The $P(\cos \vartheta, \phi)$ orientational maps of the first layer methylamine molecules are shown
4 in Figure 8 as obtained at selected chemical potentials at the five temperatures considered. For
5 comparisons, orientational maps, obtained previously on I_h ice at 200 K at the same chemical
6 potential values that are also considered here, are also shown (top row). As is seen, the
7 obtained maps are rather noisy, especially at low temperatures and low surface coverages, due
8 to the extremely slow exploration of the configurational space at these very low temperatures.
9 This fact limits the range of conclusions concerning the surface orientation of the adsorbed
10 molecules that we can reliably draw from these orientational maps. Nevertheless, it is still clear
11 that methylamine molecules prefer orientations corresponding to the $\cos \vartheta$ value of 0, i.e., to
12 the situation where the N-CH₃ bond lays parallel with the macroscopic plane of the ice surface,
13 YZ . This preference is stronger at lower surface coverages, and smoother distributions are
14 obtained at higher temperatures, when the larger thermal motion of the molecules results in
15 better statistics. Among the various orientations corresponding to $\cos \vartheta = 0$, no alignment is
16 found to be clearly preferred at every temperature and surface coverage; the maps
17 corresponding to various state points often exhibit preferences around the ϕ values of 0° , 60° ,
18 90° , 120° , and 180° . The alignments of the methylamine molecules corresponding to $\cos \vartheta = 0$
19 and these particular ϕ values are illustrated in Fig. 7. In these orientations, the methylamine
20 molecule always turns one or two of its three hydrogen bonding directions (i.e., the two N-H
21 bonds and the lone pair direction of the N atom) towards the ice surface. However, due to the
22 molecular scale roughness of the surface of amorphous ice, and to the corresponding presence
23 of pockets of locally negative curvature at the surface, the adsorbed methylamine molecules
24 located in such pockets can easily form even three hydrogen bonds with the surface waters,
25 especially at low surface coverages. The extensive H-bond formation between the first layer
26 methylamine and surface water molecules is also facilitated by the fact that surface waters on
27 amorphous ice have very weak orientational preferences, as compared to those at the surface of
28 I_h ice, as demonstrated in Fig. 7. The orientational flexibility of the surface water molecules
29 enables them to adopt orientations by which they can maximize the number of methylamine-
30 water hydrogen bonds. Further, as it was discussed in detail in our previous paper,⁴⁷ the
31 parallel alignment of the N-CH₃ bond with the ice surface promotes various relative
32 alignments, corresponding to strong dipolar interaction, of the neighboring adsorbed
33 methylamine molecules.
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5 **3.3. Energetics of the Adsorption.** To further analyze the interaction of the adsorbed
6 methylamine molecules both with each other and with the surface waters, and to characterize
7 the energetic background of the adsorption, we have calculated the binding energy of the
8 methylamine molecules belonging to the first molecular layer at the selected chemical potential
9 values at all the five temperatures considered. The binding energy of an adsorbed molecule, U_b ,
10 is defined as its interaction energy with the rest of the system (i.e., the energy cost of bringing
11 this molecule to infinite distance). Besides U_b , its contributions coming from the interaction
12 with the ice phase, and with the other methylamine molecules present in the system, denoted
13 here as U_b^{ice} and U_b^{lat} , respectively, have also been calculated.
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22 Some of the $P(U_b)$, $P(U_b^{\text{ice}})$, and $P(U_b^{\text{lat}})$ distributions obtained at 200 K are shown
23 and compared with the corresponding results on I_h ice⁴⁷ in Figure 9, while those obtained at
24 150 K, 100 K, and 50 K are shown in Figures 10.a, 10.b, and 10.c, respectively. (Similar, but
25 considerably more noisy distributions have been obtained at 20 K.) As is expected, the lateral
26 contribution to the total binding energy does not depend on the state of the ice phase. At low
27 surface coverages, the main peak of the $P(U_b^{\text{lat}})$ distribution occurs at zero energy, reflecting
28 the large fraction of isolated methylamine molecules in the adsorption layer. Besides this trivial
29 peak, another peak can be seen around -20 kJ/mol. This peak can be attributed to neighboring
30 methylamine dimers interacting with each other by strong dipolar interaction.⁴⁷ With
31 increasing surface coverages, both of these peaks shift to lower energies due to the increasing
32 background of the adsorbed methylamines, and also the relative weight of the latter, lower
33 energy peak gradually increases. The only difference seen between the $P(U_b^{\text{lat}})$ distributions
34 obtained on amorphous and I_h ices is that the relative weight of the lower energy peak is
35 slightly larger in the former case. This difference can, however, simply be explained by the
36 somewhat higher surface coverage observed on amorphous than on crystalline ice at every
37 chemical potential (see Fig. 2).
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51 On the other hand, the type of the ice phase has a great impact on the ice contribution of
52 the binding energy, U_b^{ice} . At the surface of I_h ice, the $P(U_b^{\text{ice}})$ distribution exhibits a peak
53 around -55 – -50 kJ/mol, and another one between -35 and -30 kJ/mol, attributed to the
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3 methylamine molecules forming two and one hydrogen bonds with the ice phase, respectively,
4 and with increasing surface coverage the relative weight of this latter peak increases
5 gradually.⁴⁷ At the surface of amorphous ice, this distribution is markedly shifted to lower
6 energies. Further, besides the above two positions, another peak of the distribution emerges
7 between -75 and -70 kJ/mol. This peak can be attributed to methylamine molecules forming
8 three hydrogen bonds with the ice surface. In principle, a methylamine molecule can form up
9 to three hydrogen bonds, and could orient in such a way (i.e., turning the CH₃ group straight
10 away from the ice surface) that all the three of its potential H-bonding directions (i.e., the two
11 N-H bonds and the lone pair of the N atom) points towards the ice phase. However, this
12 orientation (corresponding to the $\cos \vartheta = 1$ line of the orientational maps of Fig. 8) was found
13 not to be preferred at all both on crystalline,⁴⁷ and on amorphous ice. The reason of the lack of
14 preference for this orientation is probably that it hinders the formation of strong dipolar pairs
15 by the neighboring adsorbed methylamine molecules (or, more precisely, the formation of such
16 a dipolar pair in the first molecular layer would imply very weak interaction of the other
17 methylamine molecule with the ice phase).⁴⁷ On the other hand, the molecular level
18 corrugation of the surface of amorphous ice offers certain positions of locally negative
19 curvature (i.e., molecular size troughs), within which the adsorbed methylamine molecule can
20 still maintain all of its three possible hydrogen bonds. It is also seen from Fig. 9 that the
21 increase of the surface density leads both to the slight shift of the position of the $P(U_b^{\text{ice}})$ peaks
22 to higher energies, and to the increase of the relative weights of the peaks corresponding to
23 smaller number of hydrogen bonds. Both effects can be explained by the increasing
24 competition of the methylamine molecules at the surface.
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42 The heat of the adsorption at infinitely low surface coverage, an experimentally
43 accessible quantity, can be estimated by the mean value of the $P(U_b^{\text{ice}})$ distribution at low
44 enough surface coverages, where the lateral interaction is small enough with respect to the
45 adsorbate-adsorbent interaction. Using the lowest sampled chemical potential in every case,
46 this value turns out to be -72 kJ/mol at 200 K, and scatters between -65 and -75 kJ/mol at the
47 other temperatures considered, showing no apparent temperature dependence; its temperature
48 independent value is estimated here to be -69 ± 5 kJ/mol. By contrast, at the surface of I_h ice
49 this value was found to be only -51.3 kJ/mol,⁴⁷ emphasizing again the higher affinity of
50 methylamine to the surface of amorphous than to that of crystalline ice. Unfortunately, we are
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3 not aware of any experiment in which this value is accessed at infinitely low surface coverage.
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5 The binding energy of methylamine on amorphous ice was, however, estimated in the very
6 recent paper of Chaabouni et al.⁸³ at higher surface coverages. In a clear accordance with our
7 results, they obtained a trimodal distribution at the surface coverage corresponding to 32% of
8 the saturated monolayer, with the mean values of the peaks corresponding roughly to -35, -45,
9 and -61 kJ/mol (see Fig. 7 of Ref. 83). Similar, although somewhat lower values are obtained
10 here when considering chemical potential values corresponding to similar surface coverages
11 (e.g., -34, -52, and -71 kJ/mol at 100 K). At the lowest surface coverage considered,
12 corresponding to 15% of the saturated monolayer, Chaabouni et al. estimated the binding
13 energy to be -50 kJ/mol,⁸³ which is considerably smaller in magnitude than our estimate of
14 -69 ± 5 kJ/mol. However, our value is derived from configurations corresponding to the
15 surface coverage values of 0.18-0.36 μmol/m², which, considering our estimate of
16 12.6 μmol/m² for the saturated monolayer (see sec. 3.1), corresponds to only 1.5-3% of the
17 saturated monolayer. This one order of magnitude difference between the surface coverages
18 can largely explain the above difference between our result and the value reported by
19 Chaabouni et al. It should also be noted that Chaabouni et al. measured the surface desorption
20 rate of methylamine, and derived the binding energy distribution using several model
21 assumptions.⁸³ Nevertheless, this comparison also leaves open the possibility that the potential
22 model combination used in the present study somewhat overestimates the adhesion between
23 the ice surface and the methylamine molecules. It should also be noted that the experimental
24 value of the activation energy of the methylamine desorption reported by Chaabouni et al. as
25 well as the heat of adsorption value estimated from our simulations, considering either
26 amorphous or crystalline ice, are a factor of 2-3 larger than the speculative value of -25 kJ/mol,
27 estimated by Vinogradoff *et al.*, assuming that the desorption activation energy of methylamine
28 is identical to that of ammonia.²¹

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47 Due to the larger ice contribution, the total binding energy distribution, $P(U_b)$, is also
48 shifted to lower energies when going from crystalline to amorphous ice. Interestingly, the
49 distributions obtained at various surface coverages are rather similar to each other, indicating
50 that the weakening of the adsorbate-ice interaction is fully compensated by the increase of the
51 lateral interaction upon increasing the surface coverage. At lower temperatures, the obtained
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3 $P(U_b)$ curves exhibit two distinguishable peaks, still reflecting the presence of methylamine
4 molecules forming two and three hydrogen bonds with the surface waters.
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7 The binding energy distributions obtained at lower temperatures show the same general
8 picture, with no apparent temperature dependence of their features. The only clear effect of the
9 temperature decrease is that the distributions become more structured, and their peaks get
10 sharper. Although this effect can be explained by the decreasing weight of the entropy term of
11 the free energy of the system, it is presumably also, at least partly, due to the worsening of the
12 sampling due to the decreased mobility of the molecules at lower temperatures.
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17 Besides that of the adsorption layer, we have also investigated the energetics of the
18 methylamine molecules that are dissolved in the bulk ice phase. The bulk phase concentration
19 of these molecules is always small enough that the lateral contribution to their binding energy
20 is nearly zero. Therefore, here we only discuss the distribution of the ice contribution, U_b^{ice} .
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23 The $P(U_b^{\text{ice}})$ distribution of the dissolved molecules is shown in Figure 11 in all cases when it
24 is not affected by too large statistical noise. The distributions do not show apparent dependence
25 on the chemical potential (as the corresponding bulk ice concentration is always small enough);
26 the observed differences can rather be attributed to the poor sampling due to the small number
27 of the dissolved molecules.
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34 At 200 K, the obtained $P(U_b^{\text{ice}})$ distributions are smooth and unimodal, having their
35 peak between -80 and -85 kJ/mol. At lower temperatures, peaks corresponding to
36 methylamines forming two and three hydrogen bonds with the surrounding water molecules
37 can, in some cases, be distinguished. The overall picture is rather similar to what has been seen
38 in the first adsorbed monolayer, with a shift of the entire distributions to about -10 kJ/mol
39 lower energies. The energy of solvation at infinite dilution, obtained considering the $P(U_b^{\text{ice}})$
40 distribution in all cases when the $P(U_b^{\text{lat}})$ distribution (not shown) does not extend below
41 -5 kJ/mol, has turned out to be -74 ± 7 kJ/mol. This value is only about 5 kJ/mol deeper than
42 what is obtained in the surface monolayer, emphasizing again that at low enough surface
43 coverages methylamine molecules can be accommodated in pockets of locally negative
44 curvature of the surface, in which their local environment can be rather similar to that inside
45 the bulk ice phase.
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4. Summary and Conclusions

In this paper, we presented a detailed computer simulation analysis of the adsorption of methylamine at the surface of amorphous ice at low temperatures, some of which are relevant in studying processes occurring in the ISM. Our results clearly showed that methylamine has a strong ability of being adsorbed at such surfaces, which leads even to multilayer adsorption at high enough relative pressures. The adsorption was found to be strongly enhanced by the decrease of the temperature, thus, in the temperature range of 20-50 K, characteristic of a large part of the space, considerable surface densities can be reached even at as low bulk gas phase concentrations that occur in the ISM. It should be emphasized, however, that our simulations access only the state of thermodynamic equilibrium, but can say nothing about the kinetics of the adsorption. In other words, we found that at the low temperatures and concentrations characteristic to the ISM icy surfaces may well contain a considerable amount of adsorbed methylamine in equilibrium, but have no access to the time scale within which this equilibrium can be reached under the extreme conditions of the ISM.

When comparing our present results with those obtained earlier at the surface of crystalline (I_h) ice under similar conditions,⁴⁷ we found a considerably higher adsorption capacity of the amorphous ice surface than that of I_h ice, primarily due to the larger surface area of the amorphous phase, resulted from the corrugation of its surface. This increase of the surface area is estimated to be as large as 20% from the surface densities of the saturated monolayer, being $10.35 \mu\text{mol}/\text{m}^2$ on crystalline,⁴⁷ while about $12.5 \mu\text{mol}/\text{m}^2$ on amorphous ice. Further, besides its increased adsorption capacity, it is also found that amorphous ice, unlike I_h ice,⁴⁷ is able to dissolve a noticeable amount of methylamine. This finding is in a clear accordance with the experimental finding of Vinogradoff et al.²¹

When analyzing the orientation and energetics of the methylamine molecules forming the first molecular layer, we found that the aforementioned enhanced adsorption capacity of amorphous ice is coupled with its ability of binding methylamine molecules considerably stronger than I_h ice. Thus, due to the molecular size roughness of the surface of amorphous ice (i.e., the presence of troughs), and to the almost negligible orientational preference of the surface water molecules, the first layer methylamine molecules can easily form even three hydrogen bonds with the surface water molecules, at least at low enough surface coverages.

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3 This behavior is in a clear contrast with our earlier finding on I_h ice, where the adsorbed
4 molecules do not form more than two such H-bonds. This difference is also reflected in the
5 estimated heat of adsorption values at infinitely low surface coverage of -51.3 kJ/mol (on I_h
6 ice)⁴⁷ and -69 ± 5 kJ/mol (on amorphous ice). This latter value is rather close to the estimated
7 heat of solvation of -74 ± 7 kJ/mol in the bulk amorphous ice phase, confirming again that at
8 the rough surface of amorphous ice, consisting of water molecules with no particular pre-
9 defined orientational preferences, methylamine molecules at low surface coverages experience
10 an almost bulk-like local environment. Finally, it has to be pointed out that the heat of
11 adsorption, estimated at the surface of both I_h and amorphous ice, is considerably lower than
12 the speculative value of Vinogradoff et al. of -25 kJ/mol,²¹ revealing that the crude assumption
13 of considering this value to be identical with that of NH_3 , made in this latter study,²¹ clearly
14 represents a serious oversimplification of the real situation.
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48 **Supporting Information.** Numerical data of the calculated adsorption isotherms. This material
49 is available free of charge via the Internet at <http://pubs.acs.org>.
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Tables

Table 1. Properties of the System at the Thermodynamic State Points Where Sample Configurations Have Been Collected for Detailed Analyses.

T/K	$\mu/kJ\ mol^{-1}$	$\langle N \rangle$	p_{rel}	$I^{first}/\mu mol\ m^{-2}$	$c/mol\ dm^{-3}$
20	-47.87	6.010	3.48×10^{-57}	0.445	0
	-39.56	48.55	1.80×10^{-35}	2.94	3.96×10^{-2}
	-32.08	145.4	6.31×10^{-16}	8.58	7.94×10^{-2}
	-28.75	265.8	3.06×10^{-7}	11.2	0.1272
	-50.83	5.263	7.88×10^{-25}	0.391	0
50	-42.10	44.21	1.04×10^{-15}	3.00	1.98×10^{-2}
	-34.62	143.1	6.83×10^{-8}	9.55	0.1091
	-29.63	305.1	1.11×10^{-2}	11.5	0.1189
	-49.32	5.964	1.03×10^{-10}	0.395	3.57×10^{-2}
	-43.50	49.77	1.13×10^{-7}	3.41	3.96×10^{-2}
100	-37.68	151.4	1.23×10^{-4}	9.26	0.1208
	-31.86	305.4	0.135	11.7	0.1525
	-51.05	4.942	3.06×10^{-7}	0.354	5.55×10^{-5}
	-43.57	46.56	1.23×10^{-4}	3.20	2.58×10^{-2}
	-39.83	124.8	2.48×10^{-3}	7.46	0.1189
150	-33.59	237.7	0.368	11.4	0.3514
	-50.49	3.089	3.91×10^{-5}	0.159	1.48×10^{-2}
	-47.17	18.50	2.89×10^{-4}	1.01	6.68×10^{-2}
	-42.18	96.12	5.80×10^{-3}	5.20	0.2496
	-38.85	169.7	4.29×10^{-2}	8.67	0.5348
200	-35.53	238.1	0.317	12.1	0.7131
	-33.78	330.5	0.905	13.9	1.064
	-33.03	921.1		12.9	0.7528

Figure Legend

Figure 1. Equilibrium snapshots of the system simulated at 20 K, as obtained at four selected chemical potential values, shown both from top and side views. Water O atoms are represented by red balls, while methylamine molecules dissolved in the ice phase, being in the first monolayer at the ice surface, and being in outer molecular layers of the adsorbed phase are shown by dark blue, yellow, and cyan colors, respectively.

Figure 2. Adsorption isotherms of methylamine on amorphous ice, shown in the form of average number of molecules in the basic box as a function of the chemical potential, as obtained from our sets of GCMC simulations at the five temperatures considered. Circles, black color: $T = 200$ K, squares, red color: $T = 150$ K, up triangles, green color: $T = 100$ K, down triangles, blue color: $T = 50$ K, diamonds, orange color: $T = 20$ K. The lines connecting the points are just guides to the eye. The state points at which sample configurations have been collected for detailed analyses are marked by arrows; the corresponding chemical potential values are also indicated. The inset compares the isotherm obtained here at 200 K (filled circles) with that obtained previously at this temperature on crystalline I_h ice (Ref. 47, open circles). All data points include also the molecules that are dissolved in the bulk ice phase.

Figure 3. The chemical potential of methylamine corresponding to the point of condensation as a function of the temperature, as obtained from our GCMC simulations (filled circles). The straight line fitted to these points is also shown (dashed line).

Figure 4. Adsorption isotherms of methylamine on amorphous ice, shown in the form of surface density vs. relative pressure, as obtained from our sets of GCMC simulations at the five temperatures considered. Black circles: $T = 200$ K, red squares: $T = 150$ K, green up triangles: $T = 100$ K, blue down triangles: $T = 50$ K, orange diamonds: $T = 20$ K. The lines connecting the points are just guides to the eye. The Langmuir isotherms fitted to the 200 K, 150 K, and 100 K data are shown by dashed lines of the respective colors. The inset compares the isotherm obtained here at 200 K (filled circles) with that obtained previously at this temperature on crystalline I_h ice (Ref. 47, open circles), together with the Langmuir isotherms fitted to them. All data points include also the molecules that are dissolved in the bulk ice phase.

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4 **Figure 5.** Mass density profiles of all methylamine molecules present in the basic box (solid
5 curves) and of those forming the first monolayer at the ice surface (full circles) along the
6 interface normal axis, X , obtained at selected chemical potential values at 200 K (top panel),
7 150 K (second panel), 100 K (third panel), 50 K (fourth panel), and 20 K (bottom panel). For
8 reference, the density profile of the water molecules forming the ice phase is also shown (thick
9 dashed line). All profiles shown are symmetrized over the two interfaces present in the basic
10 box.
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17 **Figure 6.** Dissolution isotherms of methylamine in amorphous ice, shown in the form of
18 average number of dissolved molecules in the basic box as a function of the chemical potential,
19 as obtained from our sets of GCMC simulations at the five temperatures considered. Black
20 circles: $T = 200$ K, red squares: $T = 150$ K, green up triangles: $T = 100$ K, blue down triangles:
21 $T = 50$ K, orange diamonds: $T = 20$ K. The lines connecting the points are just guides to the
22 eye. The inset shows the same isotherms, in the form of bulk concentration vs. relative
23 pressure.
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31 **Figure 7.** Definition of the local frame fixed to the individual methylamine (top left) and water
32 (top right) molecules, and of the polar angles ϑ and ϕ of the surface normal vector pointing, by
33 our convention, away from the ice phase, \underline{X} , in these frames (see the text). Illustration of the
34 preferred alignments of the surface methylamine molecules relative to the surface normal
35 vector, \underline{X} (bottom left). Orientational maps of the water molecules at the surface of crystalline
36 (I_h) ice and amorphous ice, together with the illustration of the orientations preferred at I_h ice
37 (bottom right). In the orientational maps, lighter colors correspond to higher probabilities.
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44 **Figure 8.** Orientational maps of the first layer methylamine molecules at the surface of
45 crystalline (I_h) ice at 200 K (top row, Ref. 47) as well as at the surface of amorphous ice at
46 200 K (second row), 150 K (third row), 100 K (fourth row), 50 K (fifth row), and 20 K (bottom
47 row), as obtained at selected chemical potential values. In the maps, lighter colors correspond
48 to higher probabilities.
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6 **Figure 9.** Distribution of the total binding energy of the first layer methylamine molecules
7 (bottom panel), as well as its contributions coming from the interaction with the other
8 methylamine molecules in the system (middle panel) and with the ice phase (top panel), as
9 obtained at 200 K at the surface of crystalline (I_h) ice (open symbols, Ref. 47), and at that of
10 amorphous ice (full symbols) at the chemical potential values of -35.5 kJ/mol (red),
11 -42.2 kJ/mol (blue), and -47.2 kJ/mol (orange).
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17 **Figure 10.** Distribution of the total binding energy of the first layer methylamine molecules
18 (bottom panel), as well as its contributions coming from the interaction with the other
19 methylamine molecules in the system (middle panel) and with the ice phase (top panel), as
20 obtained at the surface of amorphous ice at selected chemical potential values at (a) 150 K, (b)
21 100 K, and (c) 50 K.
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27 **Figure 11.** Distribution of the binding energy contribution coming from the interaction with
28 the ice phase, as obtained for the methylamine molecules that are dissolved in the bulk
29 amorphous ice phase at selected chemical potential values at 200 K (top panel), 150 K (second
30 panel), 100 K (third panel), 50 K (fourth panel), and 20 K (bottom panel).
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Figure 1
Horváth et al.

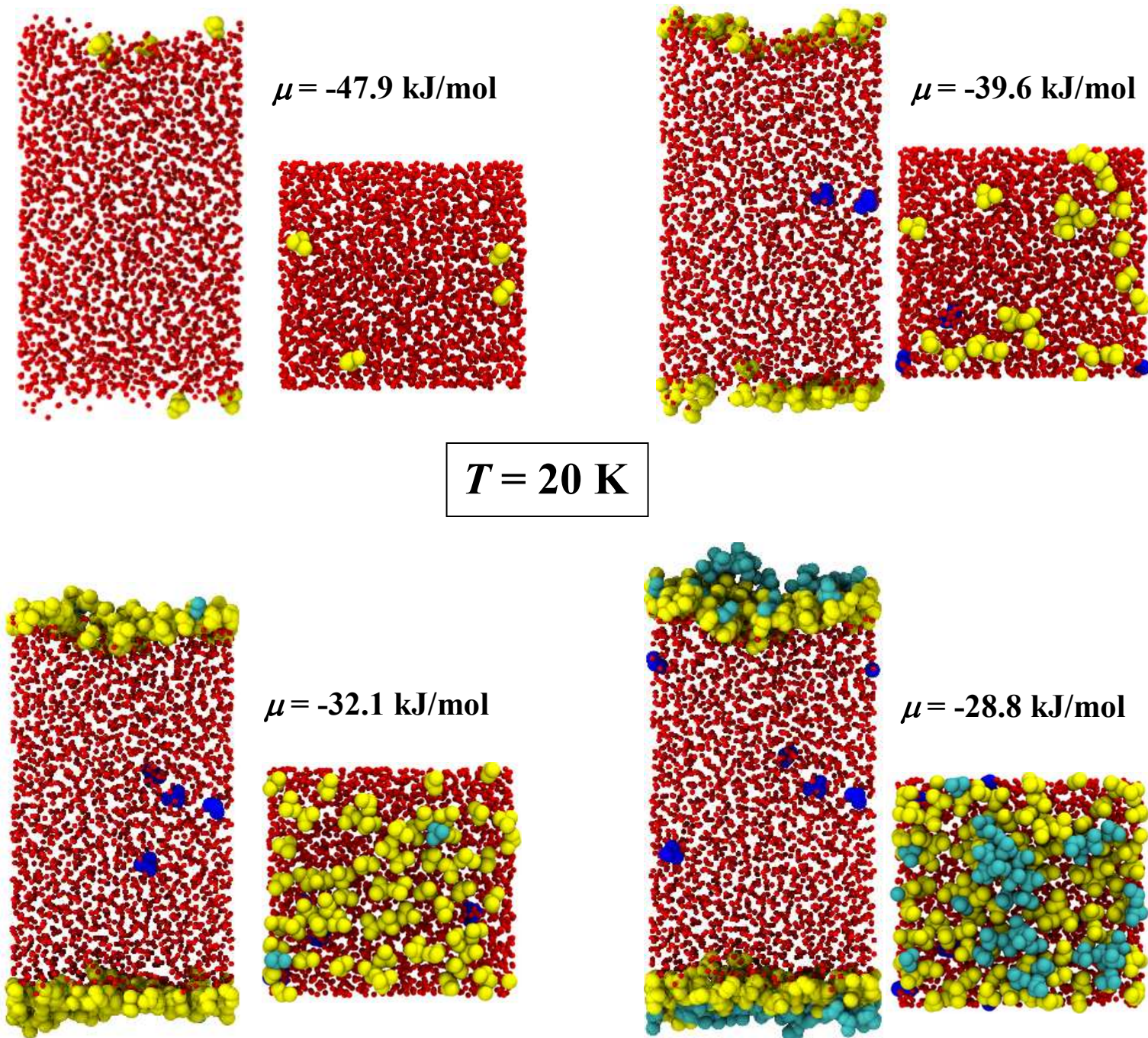


Figure 2
Horváth et al.

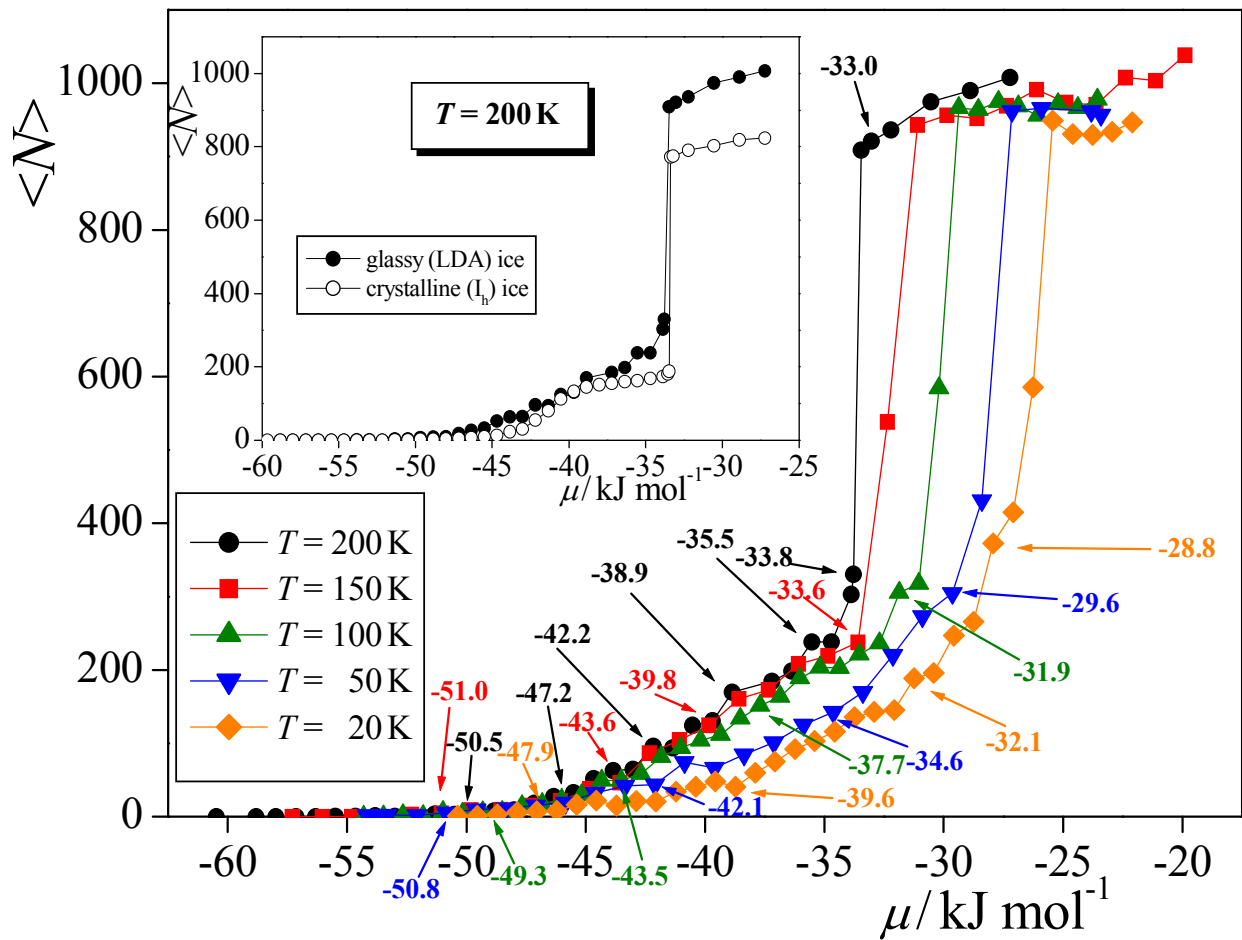


Figure 3
Horváth et al.

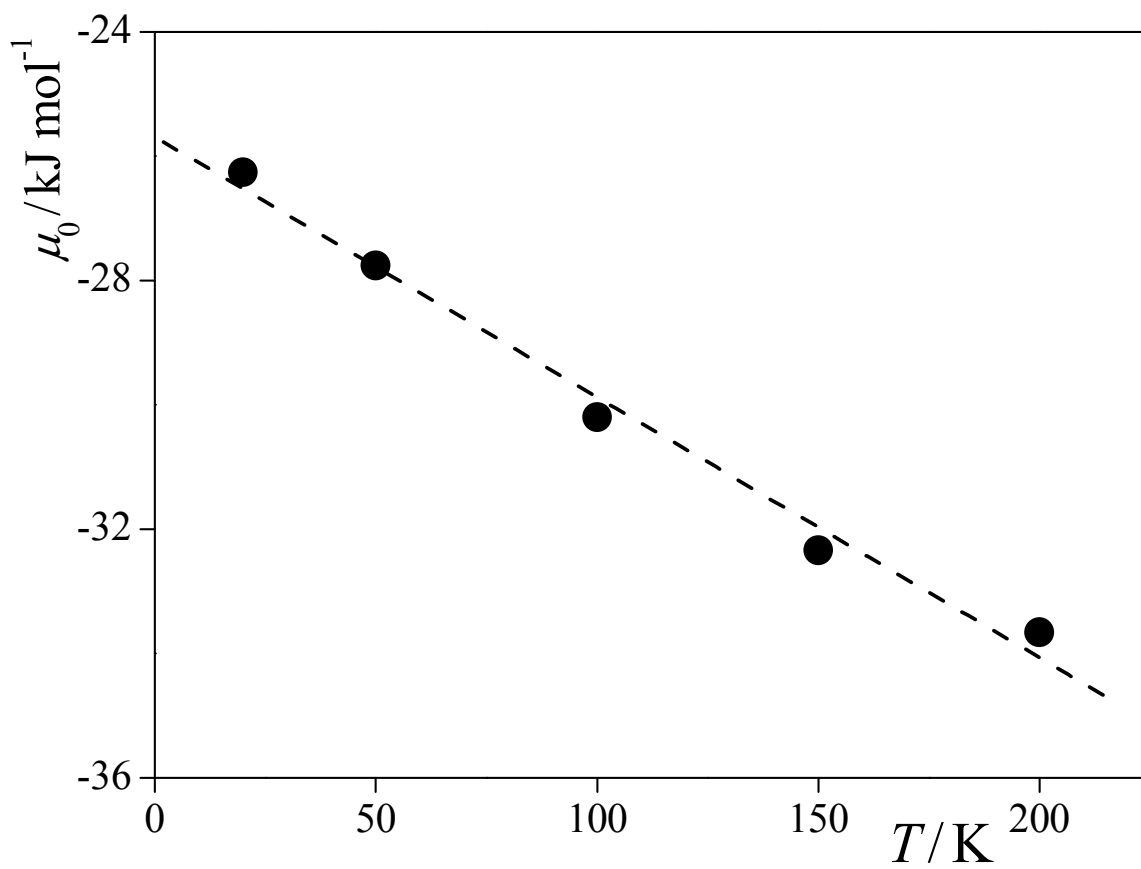


Figure 4
Horváth et al.

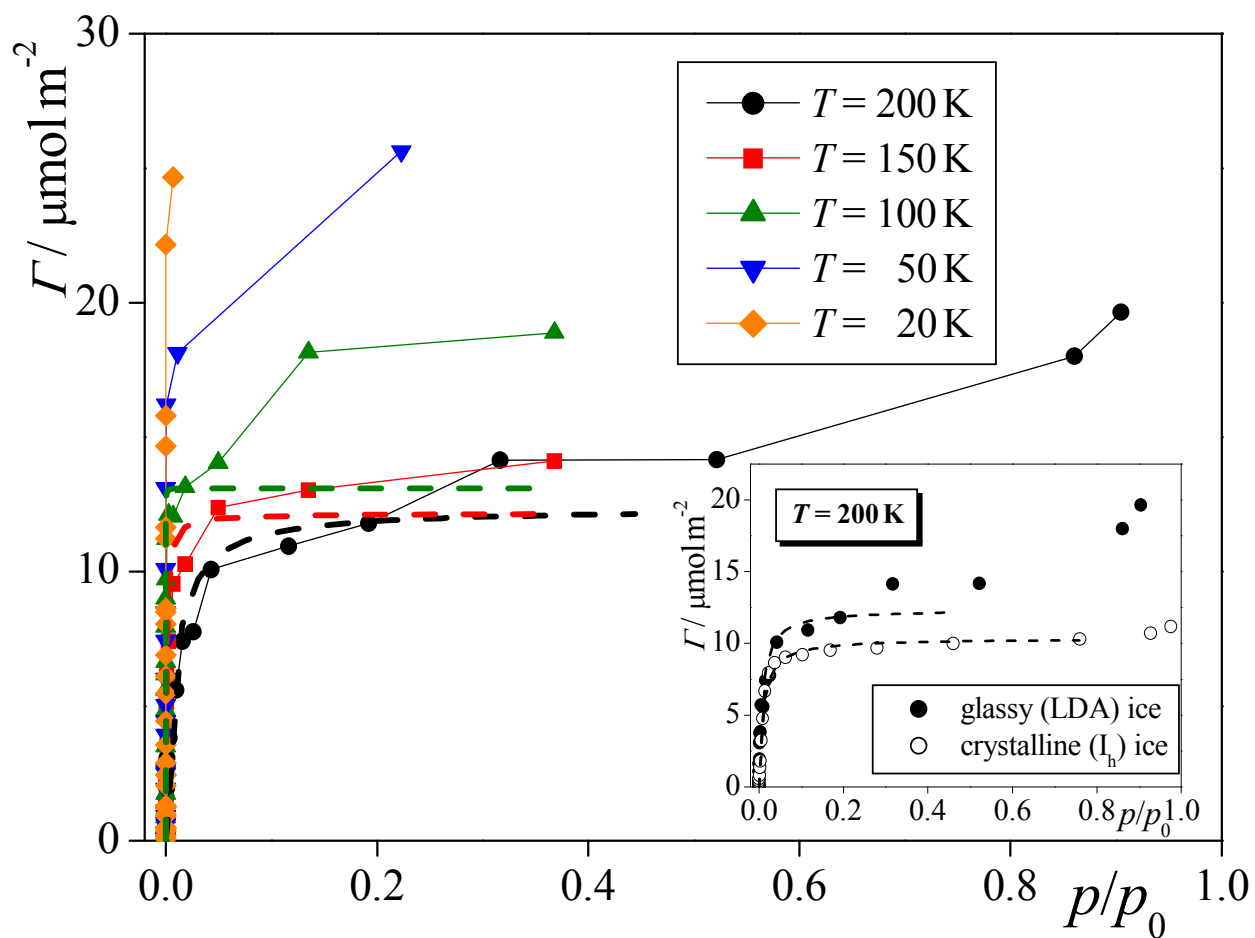


Figure 5
Horváth et al.

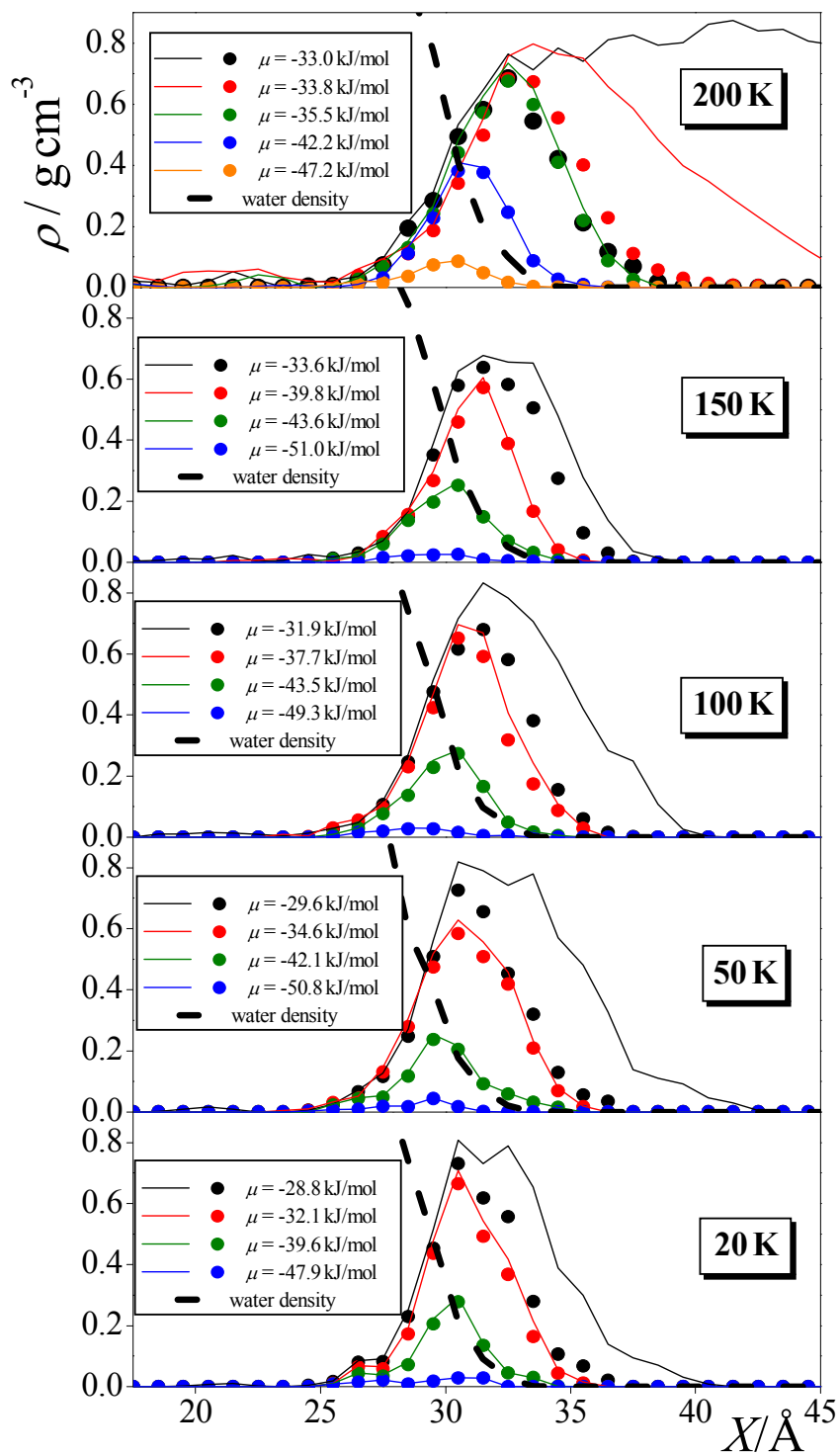


Figure 6
Horváth et al.

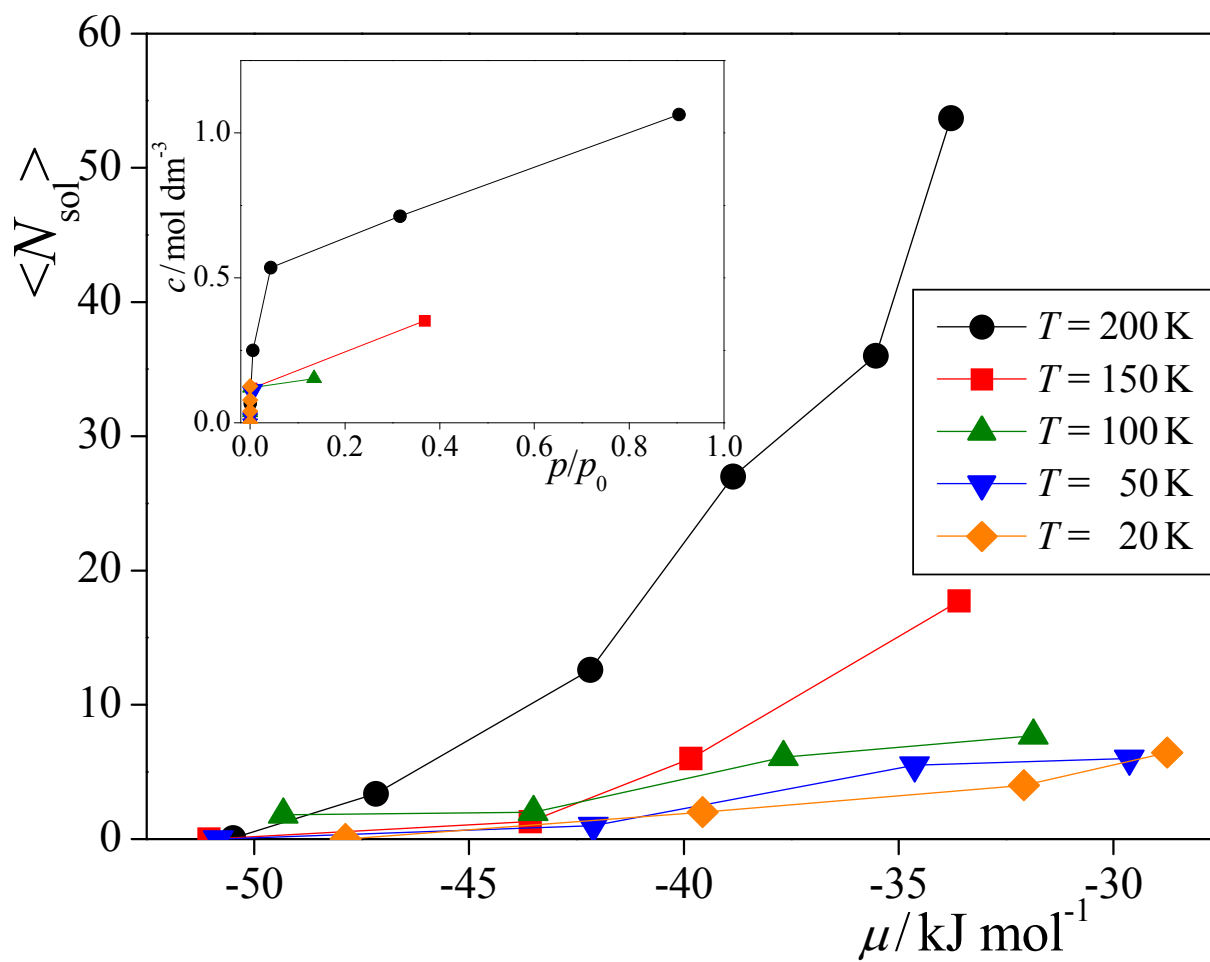


Figure 7
Horváth et al.

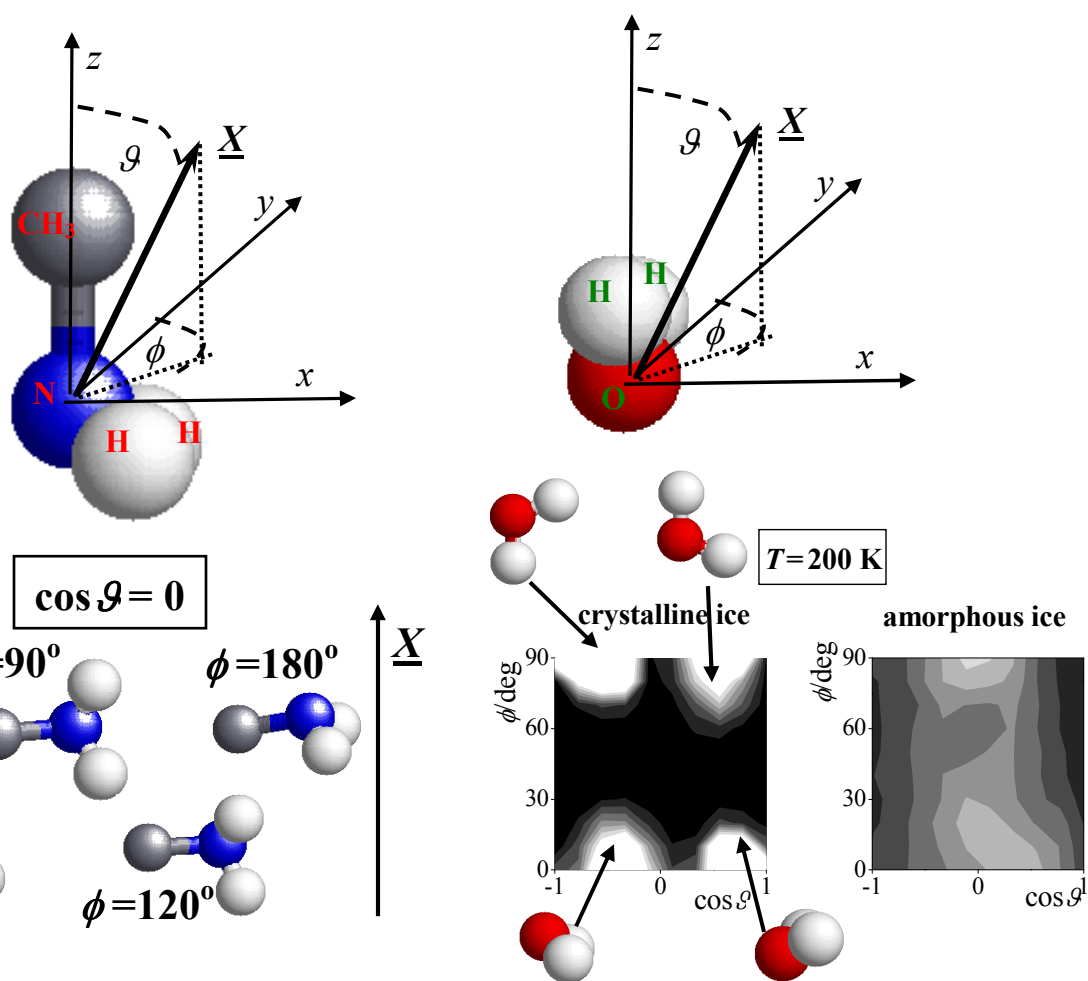


Figure 8
Horváth et al.

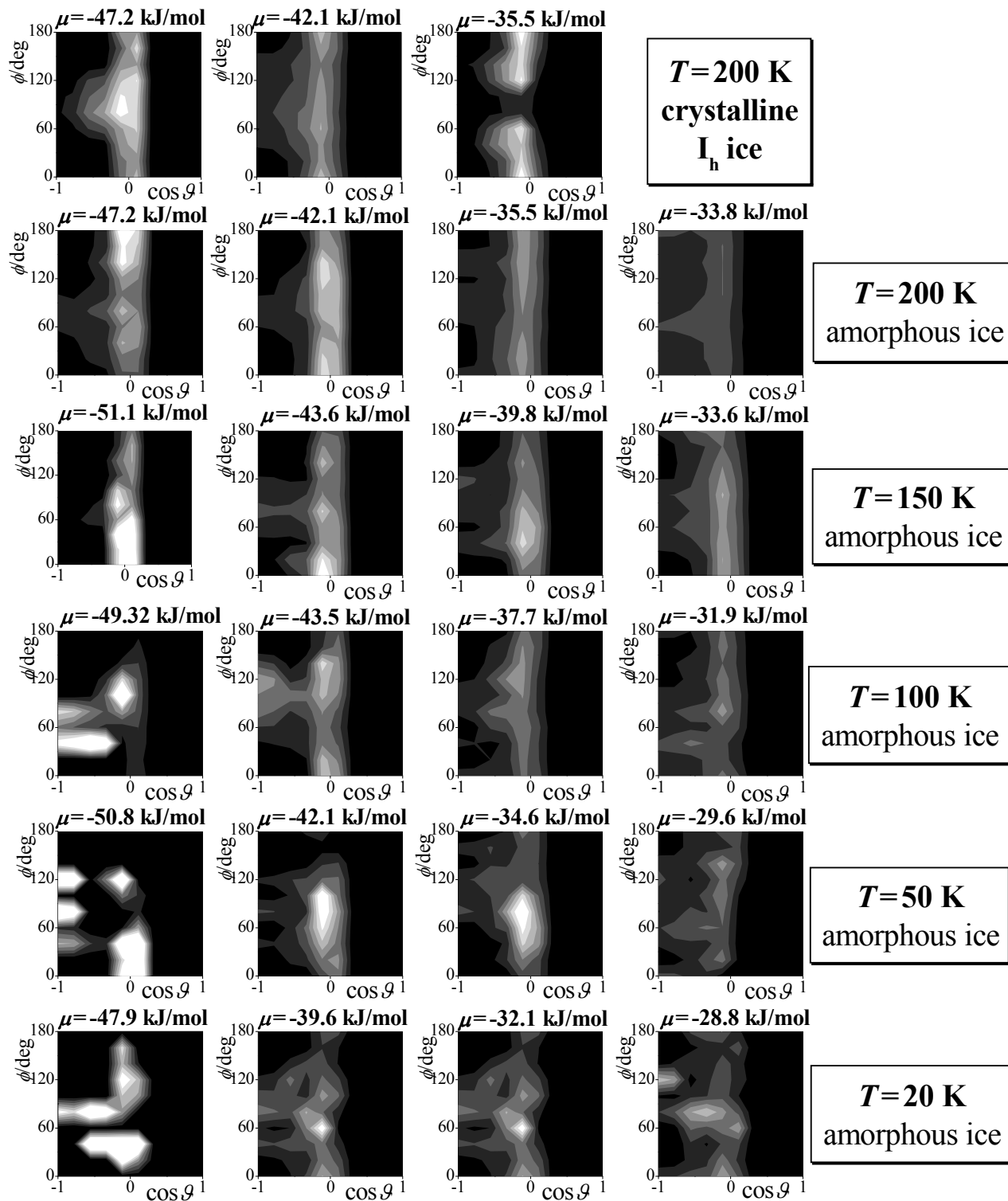


Figure 9
Horváth et al.

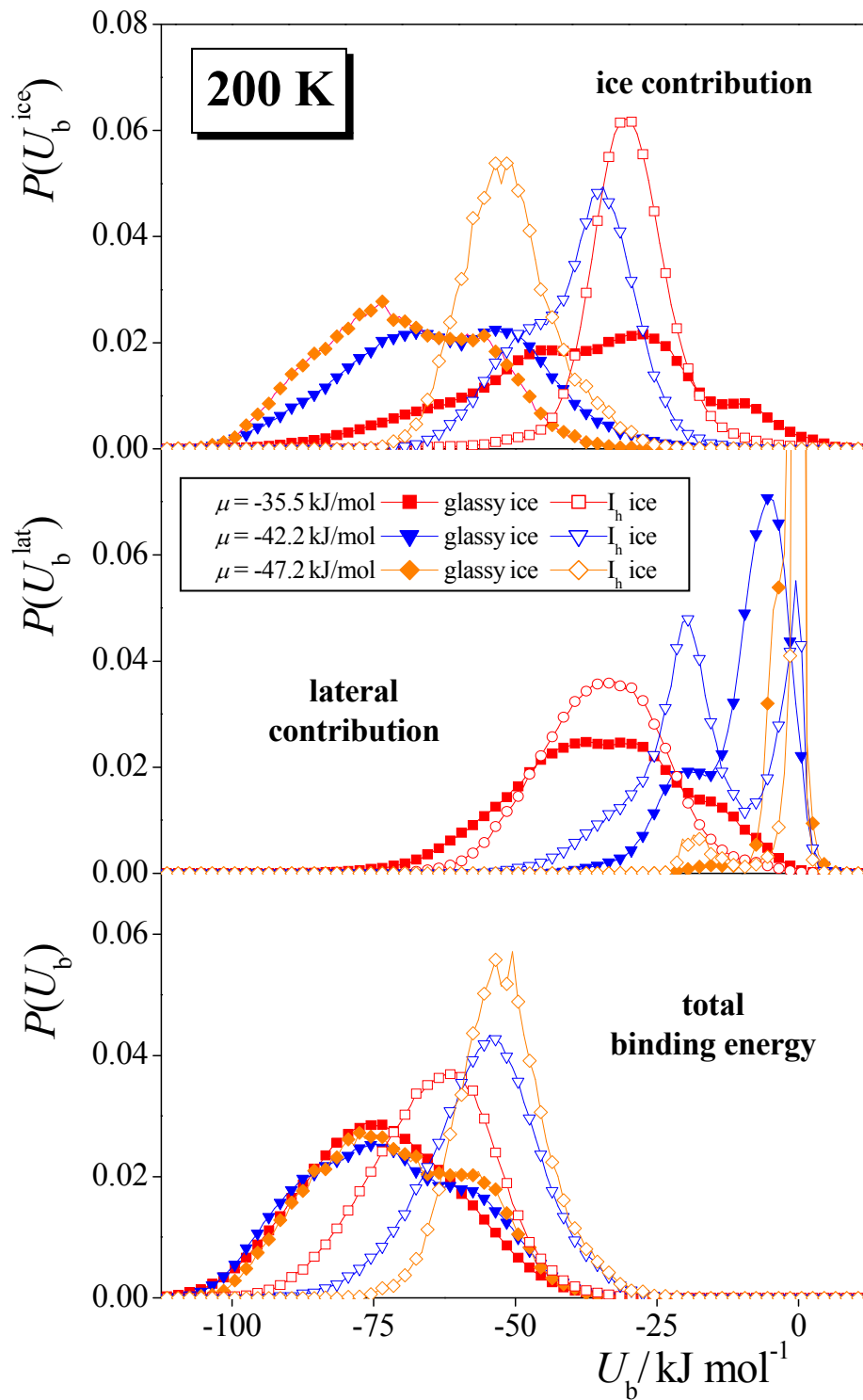


Figure 10.a
Horváth et al.

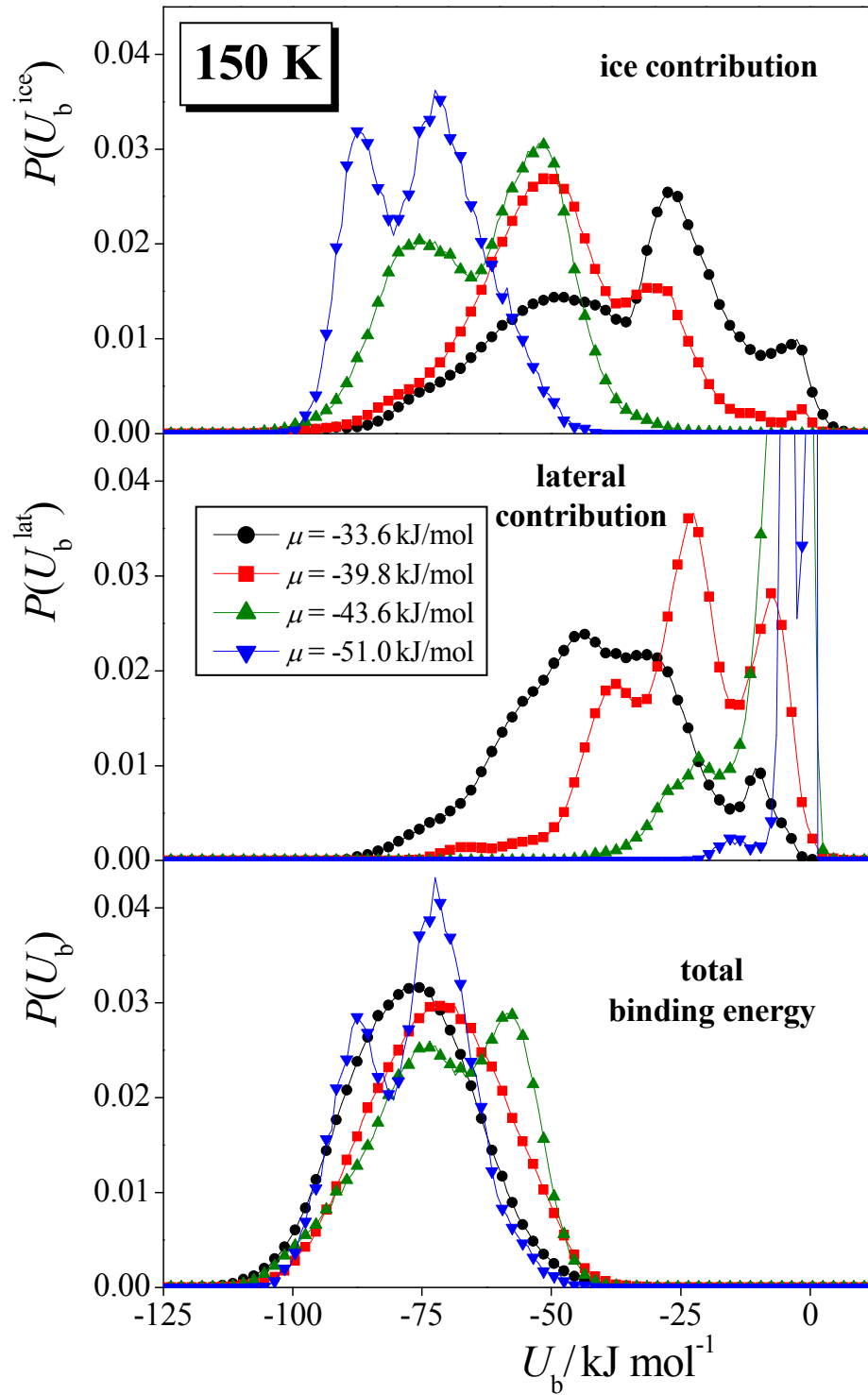


Figure 10.b
Horváth et al.

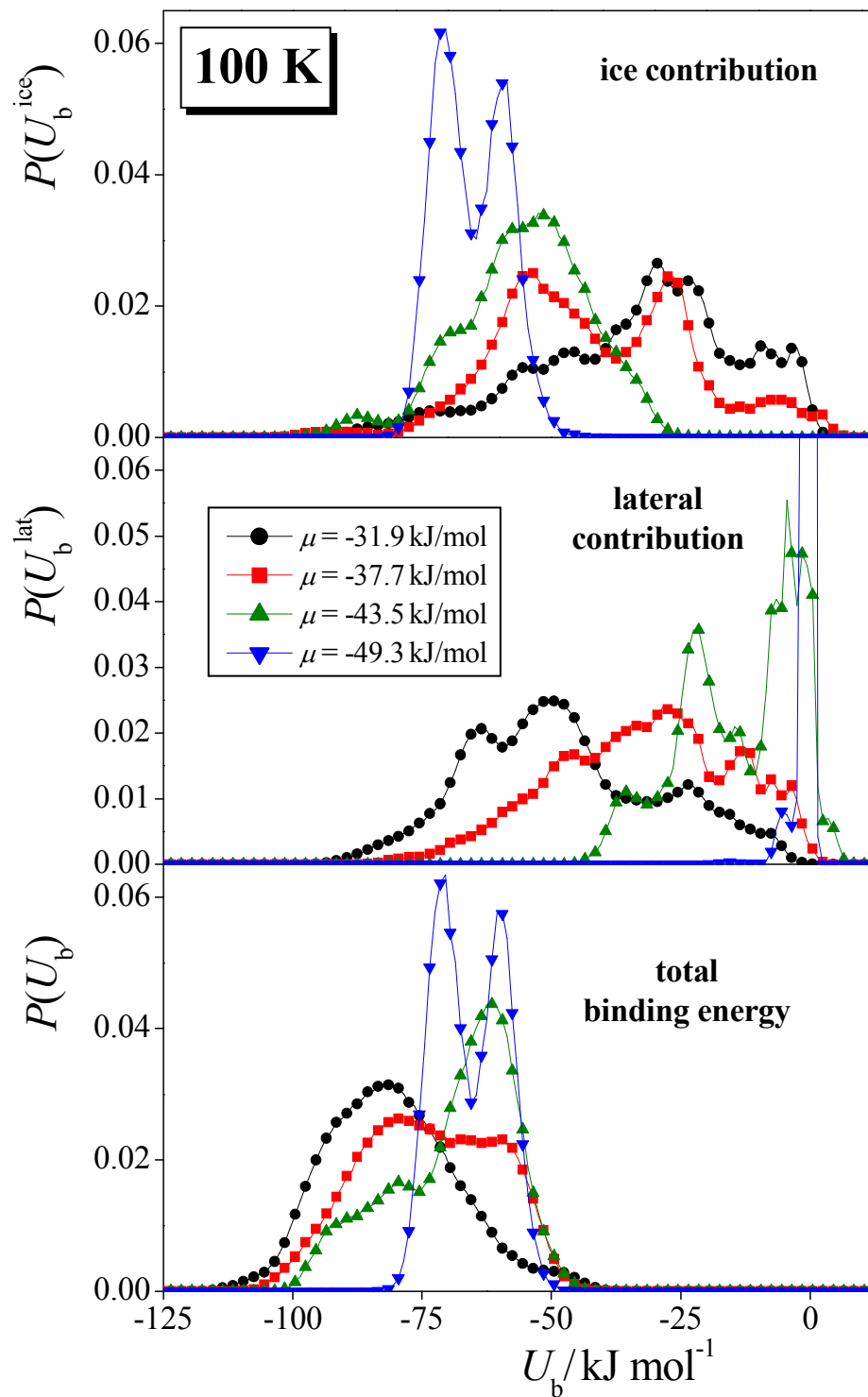


Figure 10.c

Horváth et al.

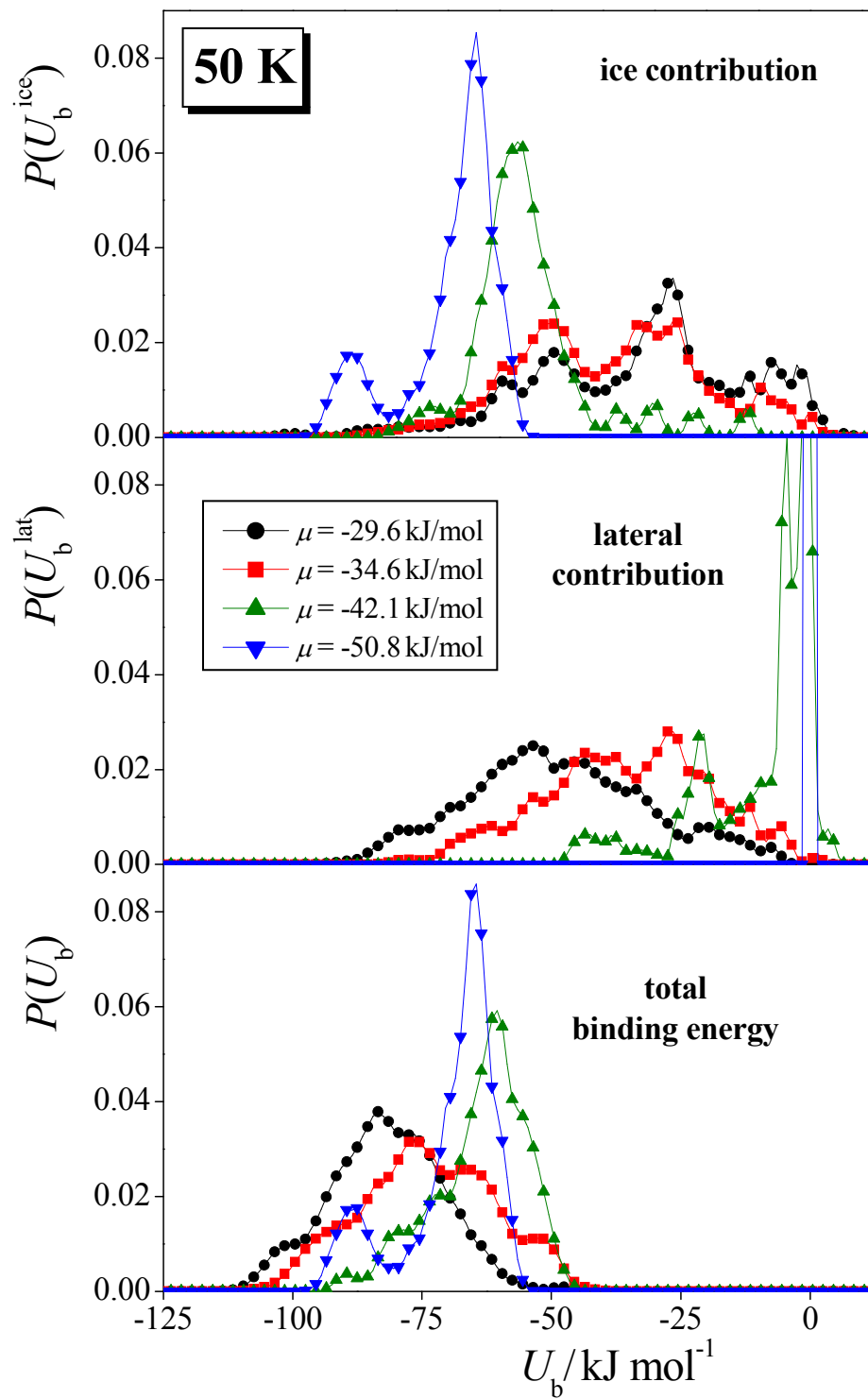
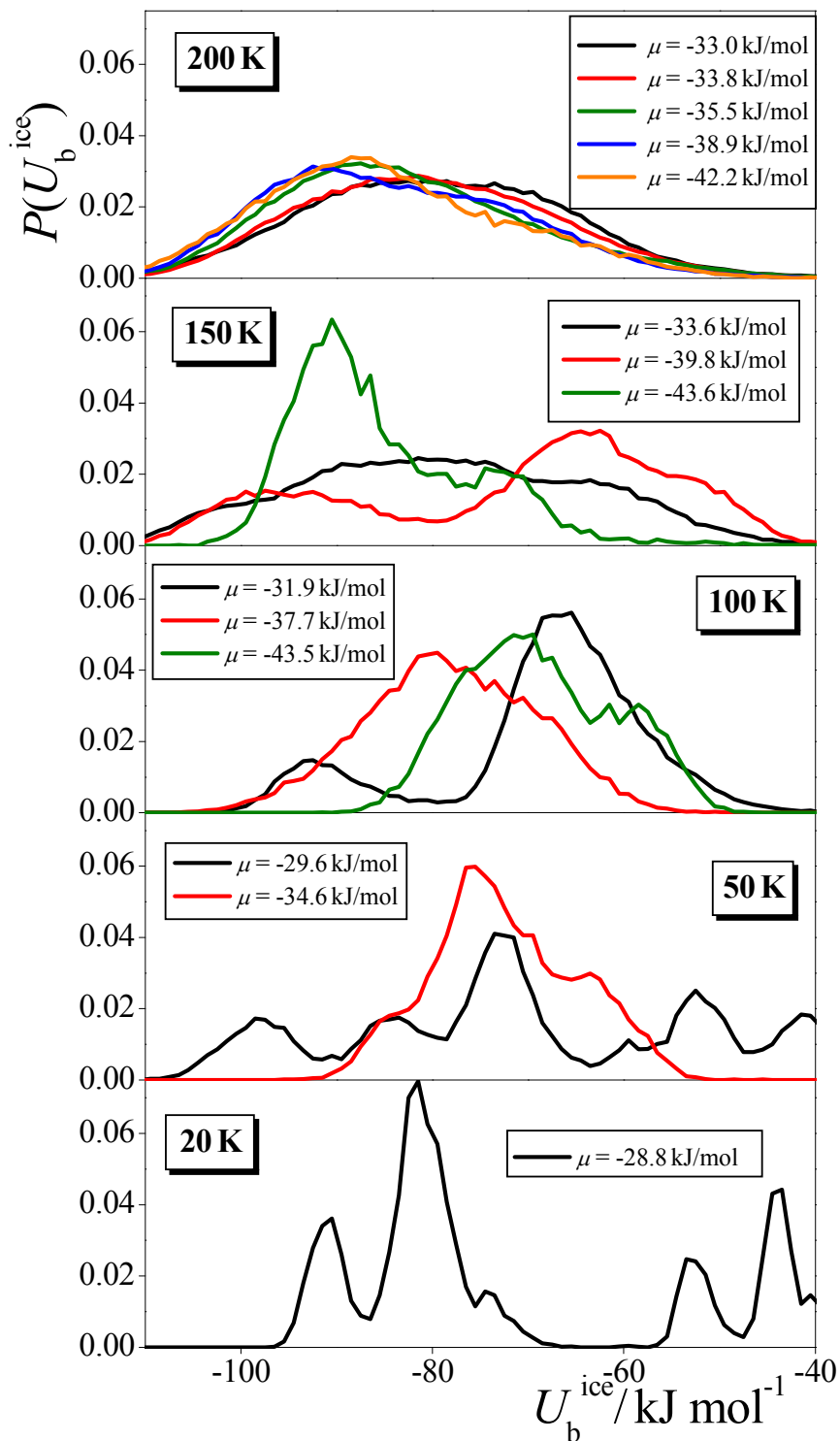


Figure 11
Horváth et al.



TOC Graphics:

