

Adsorption of acetamide on crystalline and amorphous ice under atmospheric conditions. A grand canonical Monte Carlo simulation study



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ABSTRACT

The adsorption of acetamide at the surface of crystalline (I_h) and low density amorphous (LDA) ices under tropospheric conditions is investigated by performing a set of grand canonical Monte Carlo simulations at the temperature of 200 K. Our results show that the adsorption is governed by the possibility of new H-bond formation. Further, acetamide-water and acetamide-acetamide hydrogen bonds are found to be of rather similar strengths, and hence these H-bonds are exchangeable with each other around an adsorbed molecule for practically no energy cost. In the case of monolayers being well below the saturation surface concentration, acetamide molecules prefer to stay parallel with the ice surface and form 3H-bonds with the surface waters. The energy of the adsorption at infinitely low surface concentration is estimated to be -64.5 kJ/mol on LDA and -63.7 kJ/mol on I_h ice. Increasing saturation of the surface triggers a marked change in the orientational preference of the adsorbed molecules, thus, once the interaction between the adsorbed molecules is no longer negligible (which occurs already at mildly unsaturated coverages) they prefer to stay perpendicular to the surface, forming 2 H-bonds with the ice phase and another 2 with each other. As a consequence, the ice and adsorbed phases give similar contributions to the adsorption energy at this coverage, which results in a remarkable stability of the adsorption monolayer. Indeed, after their initial rise the adsorption isotherms exhibit a plateau, corresponding to the more or less saturated adsorption monolayer, in a rather broad range of chemical potential values. The surface concentration of the saturated adsorption monolayer is estimated to be $10.2 \mu\text{mol}/\text{m}^2$ on LDA and $8.1 \mu\text{mol}/\text{m}^2$ on I_h ice. Besides adsorption, non-negligible dissolution of the acetamide molecules is found in both ice phases; however, the concentration of the dissolved molecules is still low enough that the solution exhibits ideal behaviour.

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1. Introduction

Amides are widely used as organic solvents and starting materials or intermediates in different industries. They are produced on a large scale and used extensively, for example, in the manufacture of pharmaceuticals, pesticides, fibres and adhesives [1]. Industrial use of amides results in emission of the compounds to the atmosphere during their commercial production, processing, storage, and disposal. Besides their large-scale industrial emission, important sources of amides in Earth's atmosphere include burning of biomass, wood and fossil fuels, meat cooking, vehicle exhaust, marine sources, and animal husbandry [2]. Amides can also form

in the atmosphere either by photo-oxidation of amines [3] or by accretion reaction between organic acids and ammonia or amines [4].

Acetamide (CH_3CONH_2), being one of the simplest amides, is also used on a large scale as solvent or starting material, and occurs also as intermediate in industrial syntheses. Furthermore, it is utilized as solubilizer and plasticizer, and it is also a promising phase-change material as well as a wetting and penetrating agent used in lacquers, explosives, and soldering flux. At the same time, acetamide is an important compound of several pesticides, selective herbicides and fungicides, as it can effectively control, e.g., phytopathogenic fungi (peronosporales) in potatoes, sugar beets, and other crops [5,6]. According to German Environment Agency, acetamide is classified as an organic compound with increased risk potential (OC Class I) in the report of Air Emission Reduction in the Chemical Industry Sector in Germany [7]. Similarly to other

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amides, industrial application of acetamide also results in its atmospheric emission, but its natural sources are also known. Acetamide can be found in Earth's atmosphere with a typical concentration of 8–9 pptv [8]. The main atmospheric sink of acetamide is its oxidation: its atmospheric $\cdot\text{OH}$ lifetime is estimated to be 3.3 days. [1] However, other atmospheric fates of acetamide are also plausible, among which wet deposition with subsequent hydrolysis might well be an important atmospheric loss process. Indeed, acetamide has a low vapour pressure and, due to its large permanent electric dipole moment ($\mu = 3.8 \text{ D}$) [9], it is very well soluble in water (its solubility and hydration free energy being 33.86 M [10] and -40.5 kJ/mol [11], respectively, at room temperature). In wet deposition, acetamide can be captured by crystalline (under atmospheric conditions, typically hexagonal, phase I, commonly referred to as I_h) or low density amorphous (LDA) ice grains, both present in the troposphere, through adsorption. However, this adsorption process has, to the best of our knowledge, been thoroughly characterised neither by experimental nor by computer simulation methods yet.

Computer simulation studies can well complement experimental investigations, as in a simulation an appropriately chosen model of the system of interest can be seen at atomistic resolution; such a detailed insight can thus be gained that is not accessible by any experiment [12]. Of course, the validity of the model employed needs, on the other hand, to be checked against existing experimental data. More specifically, adsorption processes can be very well studied by grand canonical Monte Carlo (GCMC) simulations [12,13], where the chemical potential of the adsorbate, μ , is kept constant and the number of its molecules is left to fluctuate. Thus, performing a set of GCMC simulations in which the chemical potential of the adsorbate is systematically varied and the number of adsorbed molecules is determined as a function of μ , the adsorption isotherm can readily be calculated. Indeed, the GCMC method has been used to characterize various adsorption processes, such as that of small molecules on covalent organic frameworks [14,15], self-assembled organic monolayers [16,17], and other carbonaceous materials [18–20], metal oxides [21,22], amorphous [23–26] and crystalline ices [24,27–32] as well as inside protein crystals [33], clay minerals [34,35], zeolites [36,37] and clathrate hydrates [38–41].

In this paper, we investigate the adsorption of acetamide at the surface of I_h and LDA ices by grand canonical Monte Carlo simulations at the tropospheric temperature of 200 K. Besides calculating the adsorption isotherms, we also investigate the possible dissolution of acetamide into the amorphous and crystalline ice phases. The energetics of the adsorption is characterised by calculating the total binding energy of the acetamide molecules directly attached to the ice surface, as well as the contributions of the binding energy given by the ice phase and by the other adsorbed molecules. The orientational preferences of the first layer molecules are also discussed in detail. The differences occurring in the adsorption process at different surface coverages are also addressed.

The paper is organised as follows. In Section 2 the details of the calculations performed are given. The resulting adsorption isotherms and the properties of the adlayer are discussed in detail in Sections 3 and 4, respectively. Finally, in Section 5 the main conclusions of this study are summarised.

2. Computational details

To investigate the adsorption of acetamide at the surface of amorphous (LDA) and crystalline (I_h) ices, grand canonical Monte Carlo simulations have been performed at 15 different acetamide chemical potential (μ) values with both ice phases. The μ values considered range from those corresponding to practically no acet-

amide molecules in the basic box to the presence of condensed phase acetamide. The μ values of the simulations as well as the mean number of the acetamide molecules found in the basic box, $\langle N \rangle$, are collected in Table 1. The simulations have been performed at the tropospheric temperature of $T = 200 \text{ K}$. The X, Y and Z edges of the rectangular basic box have been 100 Å, 35.926 Å, and 38.891 Å, respectively, X being the interface normal axis. The ice phase has consisted of 2880 water molecules. Standard periodic boundary conditions have been applied.

Acetamide molecules have been modelled by the OPLS force field [42], which has successfully been applied earlier to calculate the hydration free energy difference of acetamide from that of acetone and urea [43]. Water molecules have been described by the OPLS-compatible TIP4P potential [44]. According to these models, all molecules are rigid and planar, and the CH_3 group of acetamide is treated as a united atom [42]. In the water model, the negative fractional charge is displaced from the O atom along the bisector of the H–O–H bond to a non-atomic interaction site, M [44]. Further, the energy of the system is assumed to be pairwise additive, i.e., the total potential energy of the system is simply regarded to be the sum of the interaction energies of all molecule pairs. The interaction energy of a molecule pair is calculated as the sum of the Lennard-Jones and charge-charge Coulomb contributions of all pairs of their interaction sites. The Lennard-Jones distance and energy parameters (σ and ϵ , respectively) and fractional charges (q) of the potential models considered are collected in Table 2, while the bond lengths and bond angles of these rigid models are listed in Table 3. According to the original parametrization of these models, [42,44] all interactions have been truncated to zero beyond the centre-based cut-off distance of 12.5 Å.

The simulations have been performed with the program MMC [45]. In the simulations, particle displacement and insertion/deletion attempts have been performed in alternating order. In a particle displacement step, a randomly chosen molecule has been attempted to be randomly translated to a maximum distance of 0.25 Å and randomly rotated around a randomly chosen space-fixed axis by no more than 15° . In an insertion/deletion step either, by 50% probability, a new acetamide molecule has been attempted to be inserted into, or a randomly chosen acetamide molecule has been tried to be removed from the system. Insertion/deletion attempts have been done according to the cavity biased scheme of Mezei [46,47]. Thus, insertions have only been attempted into pre-existing cavities of the minimum radius of 2.5 Å. Suitable cavities have been searched for along a $100 \times 100 \times 100$ grid, regenerated after every 10^6 Monte Carlo steps. Trial particle displacement and insertion/deletion moves have been accepted or rejected according to the standard Metropolis criterion [12,48] and to the cavity biased scheme [46,47], respectively. The probability of finding a cavity, P_{cav} , a quantity required by the cavity biased algorithm [46,47] has been estimated simply as the ratio of the number of suitable cavities found and grid points checked. This way, typically at least 10% and 0.01% of the particle displacement and insertion/deletion attempts have been successful.

The crystalline phase of ice has simply been generated by arranging 2880 water molecules in 18 layers along the X axis according to the geometry of the I_h crystal in such a way that the free surface corresponds to the (0001) cut of I_h ice. In preparing the LDA phase of ice, the I_h crystal has been thermalised at 300 K, 350 K, and again at 300 K by performing 10^8 , 2×10^8 , and 10^8 Monte Carlo steps, respectively, and subsequently quenched at 200 K in an additional, 10^8 Monte Carlo steps long run. The starting configuration of each run has been created by randomly placing an acetamide molecule above the respective ice phase. The systems have been equilibrated in $2 \times 10^9 - 10^{10}$ Monte Carlo steps long runs, until the number of acetamide molecules has started fluctuating around its equilibrium value. Then, in the production stage,

Table 1Adsorption and dissolution isotherms of acetamide on LDA and I_h ices, as obtained from our simulations.

$\mu/\text{kJ mol}^{-1}$	p/p_0	LDA			I _h		
		$\langle N \rangle$	$\Gamma/\mu\text{mol m}^{-2}$	c/mM	$\langle N \rangle$	$\Gamma/\mu\text{mol m}^{-2}$	c/mM
-62.08	1.67×10^{-4}	0.0107	6.35×10^{-4}	0	0.0528	3.14×10^{-3}	0
-56.26	5.52×10^{-3}	0.2749	1.63×10^{-2}	0	0.3382	2.01×10^{-2}	0
-52.93 ^a	4.08×10^{-2}	2.326	7.96×10^{-2}	19.0	2.517	0.150	0
-52.10	6.72×10^{-2}	6.002	0.357	0	6.289	0.374	0
-51.27	0.111	10.30	0.599	4.1	12.98	0.771	18.6
-50.44 ^b	0.183	27.11	1.49	41.5	66.58	3.96	18.6
-49.61	0.301	53.07	3.11	14.7	119.1	7.08	18.6
-49.11	0.407	121.1	7.13	20.1	126.7	7.53	18.6
-48.78 ^c	0.497	129.3	7.58	33.9	133.3	7.92	33.8
-48.44	0.607	143.5	8.23	95.9	134.0	7.96	18.6
-48.11	0.741	151.5	8.83	57.1	140.6	8.36	19.2
-47.78 ^d	0.905	177.5	10.4	44.0	146.0	8.68	56.4
-47.45 ^e		557.0		96.3	525.2		36.3
-46.28		572.7			522.9		
-45.45		567.5			522.2		

^a system I ^b system II ^c system III ^d system IV ^e system V.**Table 2**

Interaction parameters of the molecular models used.

molecule	site	$\sigma/\text{\AA}$	$\varepsilon/\text{kJ mol}^{-1}$	q/e
acetamide	CH ₃	3.910	0.670	0.000
	C	3.750	0.440	0.380
	O	2.960	0.879	-0.380
	N	3.250	0.712	-0.666
	H	-	-	0.333
water	O	3.154	0.649	0.000
	H	-	-	0.520
	M ^a	-	-	-1.040

^a Non-atomic site, located along the bisector of the H-O-H angle.

the mean number of acetamide molecules in the basic box, $\langle N \rangle$, has been averaged over 2×10^9 equilibrium configurations. For detailed analyses, 2500 sample configurations, separated from each other by 10^6 Monte Carlo steps long trajectories, have been saved from an additional 2×10^9 steps long run at selected chemical potential values. At all other chemical potentials considered, 1000 sample configurations, separated by 10^6 Monte Carlo steps each, have been saved for calculating the average number of acetamide molecules dissolved in the bulk ice phase. Equilibrium snapshots of the systems consisting of both LDA and I_h ice are shown in Fig. 1 both in side and top views, as obtained from the simulations at selected chemical potentials.

To distinguish between the acetamide molecules that are dissolved in the bulk ice phase, attached to the ice surface forming the first adsorbed molecular layer, and pertaining to outer molecular layers, we have applied the identification of the truly interfa-

cial molecules (ITIM) algorithm [49]. In an ITIM analysis, particles being at the surface of their phase are searched for by moving a spherical probe along a set of grid lines perpendicular to the macroscopic plane of the interface. Once the probe touches the first molecule of the phase of interest along a certain grid line, it is stopped, the next grid line is considered, and the molecule touched is marked as being interfacial (as it is “seen” by the probe from the opposite phase). At the end of this procedure, the full set of interfacial molecules is identified [49].

In the present work, we performed a two-step ITIM procedure [23] using a probe sphere of the radius of 2 Å and a grid spacing of 0.5 Å. In the first step, the interfacial water molecules have been identified by moving the probe from outside the ice phase, determining thus the surface of the ice slab at both sides. Acetamide molecules that are found between these two surfaces have been considered as being dissolved in the ice phase, and have been disregarded in the next step. In the second step, the probe has started from the bulk ice phase, and the surface layer of the adsorbed acetamide molecules has been identified. Finally, acetamide molecules identified neither as being dissolved nor as being interfacial have been marked as belonging to an outer molecular layer of adsorbed acetamide.

Finally, in all analyses the results have been averaged not only over the sample configurations collected, but also over the two ice surfaces present in the basic box.

3. Adsorption and dissolution isotherms

The mean number of acetamide molecules in the basic box, $\langle N \rangle$, is plotted in Fig. 2 against the acetamide chemical potential, μ , as

Table 3

Geometry parameters of the molecular models used.

molecule	bond	bond length (Å)	angle	bond angle (deg)
acetamide	CH ₃ -C	1.507		
	C=O	1.248		
	C-N	1.380		
	N-H	0.990		
water			C-C=O	121.4
			N-C=O	119.3
			H-N-H	120.2
	O-H	0.9572		
	O-M	0.1577		
			H-O-H	104.52

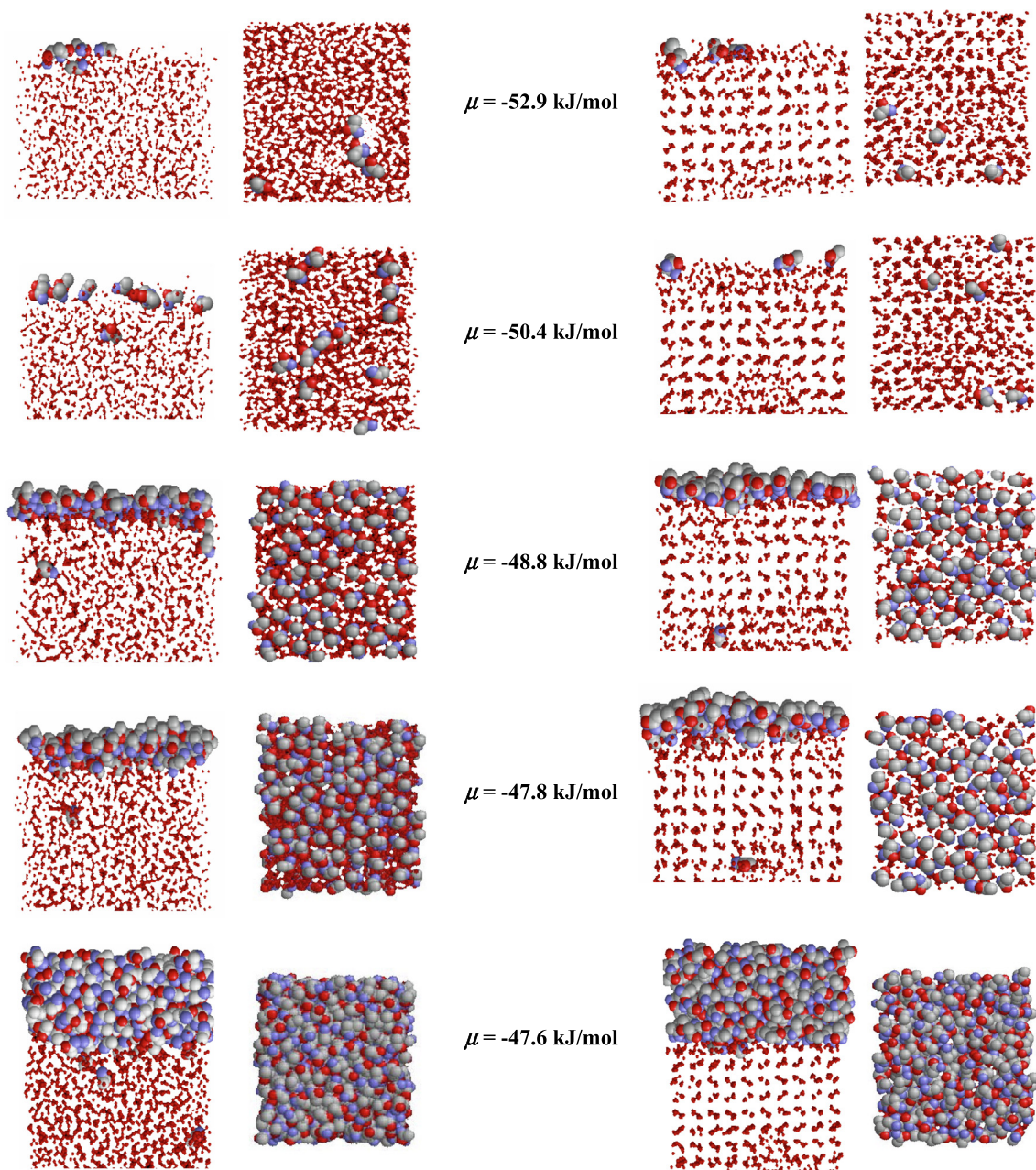


Fig. 1. Surface portion of an equilibrium snapshot of the systems simulated containing LDA (left) and I_h (right) ices, as obtained at five selected chemical potential values. The surface portion of the systems are shown both from side view (left column for both ices) and from top view (right column for both ices). The C, O and N atoms of the acetamide molecules are represented by grey, red and blue balls, respectively, while the water O atoms are shown by red dots. H atoms are omitted from the snapshots for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

obtained with both ice phases considered. Since practically no acetamide molecule has been found in the vapour phase, and only a small fraction of the molecules has been dissolved in the ice phase, these data can be regarded as relatively good estimates of the adsorption isotherms. At low μ values the curves exhibit an exponential increase (as emphasized in the inset of Fig. 2, showing the same data on a logarithmic scale), which turns into a plateau around the μ value of about -49 kJ/mol. The existence of this plateau in quite a broad μ range suggests that the adsorbed acetamide molecules form a rather stable monolayer here. The plateau is followed by a sharp jump of the curve, beyond which the basic box gets filled with acetamide. This jump marks the condensation of acetamide; the chemical potential value corresponding to the point of condensation, μ_0 , is estimated to be -47.61 kJ/mol. It should be

noted that while in the case of I_h ice the plateau extends up to the point of condensation, in the case of LDA ice the isotherm exhibits a rapid increase in a narrow μ range, evidencing the occurrence of at least traces of multilayer adsorption right below the point of condensation.

To further analyse the adsorption of acetamide at the surface, and its dissolution in the bulk of the two ice phases, we have determined the mean number of dissolved acetamide molecules, $\langle N_d \rangle$, and converted the $\langle N \rangle$ vs. μ data to the adsorption and dissolution isotherms. Fig. 3 shows the adsorption isotherms in the Γ vs. p_{rel} form, where Γ is the surface concentration of acetamide:

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

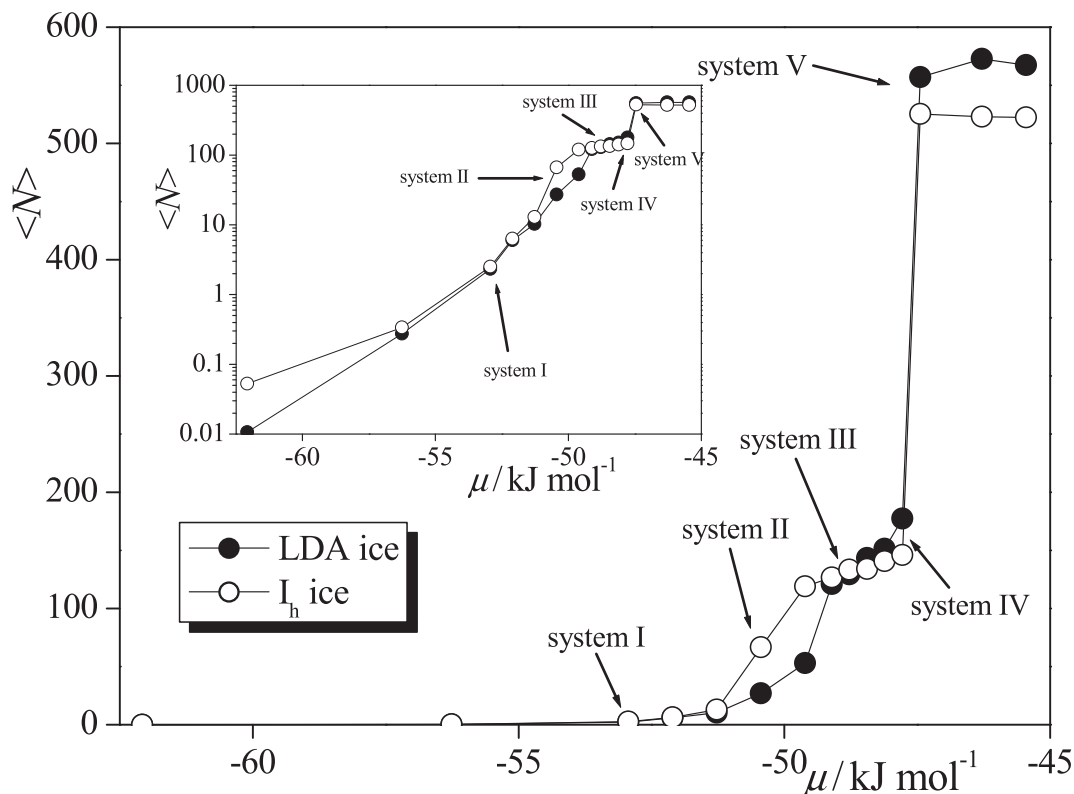


Fig. 2. Number of acetamide molecules in the basic box, obtained on LDA (filled symbols) and I_h (open symbols) ices, as a function of the acetamide chemical potential. The lines connecting the points serve only as guides to the eye. To demonstrate the initial exponential increase, the inset shows the same data on a logarithmic scale. The systems chosen for detailed analyses are also indicated.

and p_{rel} is the relative pressure, i.e., the pressure, p , normalized by that of the saturated vapour, p_0 , calculated as [21].

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

k_B being the Boltzmann factor. (The factor of 2 in the denominator of eq. (1) accounts for the two ice surfaces present in the basic box.) It should be noted that, since p_0 is the pressure corresponding to the point of condensation, p_{rel} loses its meaning above 1, thus, the Γ vs. p_{rel} isotherm has only been calculated up to $p_{\text{rel}} = 1$. The dissolution isotherms are shown in the inset of Fig. 3 in the form of the bulk phase concentration of acetamide, c , as a function of its chemical potential, μ . The values of p_0 , Γ and c are also included in Table 1.

As is seen, the adsorption isotherms exhibit a rise of increasing steepness before reaching the plateau of the saturated monolayer. This shape is markedly different from that of the Langmuir isotherm, [50] which exhibits a rise of continuously decreasing steepness. The markedly non-Langmuir behaviour of the adsorption isotherms clearly indicates the presence of strong lateral interaction between the adsorbed molecules.

Due to the rather small number of dissolved acetamide molecules, the obtained $c(\mu)$ dissolution isotherms are rather noisy. Nevertheless, the obtained data exhibit a rise of increasing steepness, suggesting that c increases exponentially with μ (and, hence, linearly with p). Considering the basic physico-chemical relation of,

$$\mu = \mu_0 + RT \ln a \quad (3)$$

where $a = cy(c)$ is the activity, while y is the (concentration dependent) activity coefficient, this more or less exponential rise of c with

μ suggests that the concentration of dissolved acetamide in the ice phases at this temperature is still low enough to keep the activity coefficient close to unity. However, due to the rather large statistical noise affecting the $c(\mu)$ data, we refrain here from drawing more definite conclusion concerning the functional form or details of the shape of the dissolution isotherms.

Interestingly, the dissolution isotherms obtained for LDA and I_h ices agree, within the (rather large) statistical noise with each other. Acetamide molecules dissolved in I_h ice have to locally destroy the hexagonal crystalline order of the water molecules (as seen also from the corresponding snapshots of Fig. 1), hence, the observed spontaneous dissolution of acetamide implies that the hydration free energy of acetamide (being -40.5 kJ/mol at room temperature [11]) covers the lattice energy of I_h ice even at as low temperature as 200 K.

4. Properties of the adsorption layer

To analyse the properties of the adsorption layer, we have performed detailed analyses at five selected chemical potential values, indicated in Table 1. Thus, system I ($\mu = -52.93$ kJ/mol) corresponds to the situation when only a few, presumably isolated acetamide molecules are adsorbed. Systems II ($\mu = -50.44$ kJ/mol) and III ($\mu = -48.78$ kJ/mol) correspond to a largely unsaturated and to a more or less saturated adsorption monolayer, respectively, while system IV ($\mu = -47.78$ kJ/mol) is the state just preceding condensation – at least on LDA ice, traces of multilayer adsorption are expected to occur here. Finally, in system V ($\mu = -47.45$ kJ/mol), acetamide is already in condensed state. Snapshots of these systems are shown in Fig. 1; the data points corresponding to them are also indicated in Figs. 2 and 3.

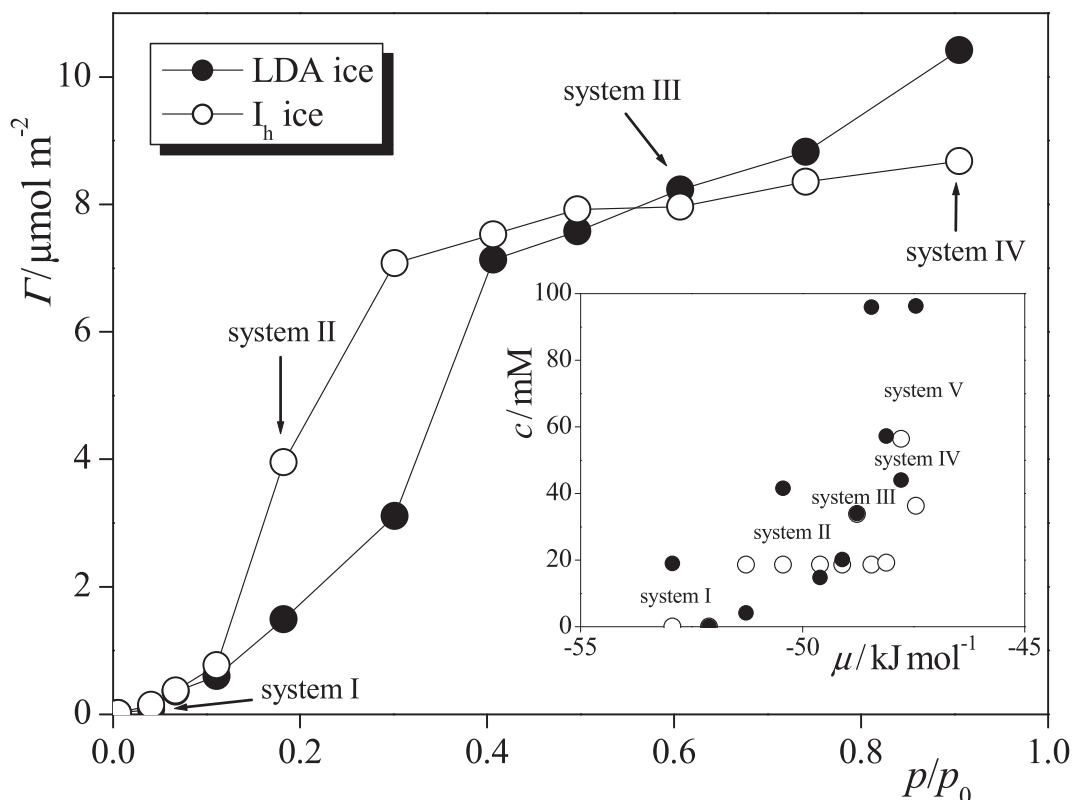


Fig. 3. Adsorption isotherm of acetamide on LDA (filled symbols) and I_h (open symbols) ices in the Γ vs. p_{rel} form, as obtained from our simulations. The lines connecting the points serve only as guides to the eye. The inset shows the dissolution isotherms of acetamide in the two ice phases. The systems chosen for detailed analyses are also indicated.

4.1. Density profiles

The profiles of the molecular number density, ρ , of the acetamide molecules forming the first layer at the ice surface as well as of all acetamide molecules along the surface normal axis, X , are shown in Fig. 4 as obtained in systems I–V at both ice phases considered. The number density profile of the water molecules in this region is also shown for reference, while the water number density profiles within the LDA and I_h ice phases are compared in the inset of the figure.

As is seen, in systems I–III and, in the case of I_h ice, also in system IV the number density profile of all acetamide molecules practically coincides with that of the first layer molecules, confirming that in these states, corresponding to the initial rise or the plateau part of the isotherms, the adsorption layer is indeed strictly monomolecular. Further, in system IV on LDA ice, the density peak of the first layer acetamide molecules is somewhat narrower than that of the entire adsorption layer, confirming also that, at the surface of LDA ice, the occurrence of traces of multilayer adsorption indeed precedes condensation. In system V, the basic box is already filled with condensed phase acetamide. As it is clearly seen, the order of the subsequent molecular layers in I_h ice (see the inset of Fig. 4) clearly induces a layering order also in the acetamide phase.

It is also seen that the density peak of the first layer molecules in system IV and, in the case of I_h ice also in system III is rather similar to that of system V. This finding confirms that the adsorption monolayer is more or less saturated at the plateau part of the isotherms. The surface concentration of the saturated monolayer can be estimated by integrating the density peak of the first layer molecules in system V, i.e., in the case of condensed acetamide. This value is resulted in 10.2 $\mu\text{mol/m}^2$ and 8.1 $\mu\text{mol/m}^2$ for LDA

and I_h ice, respectively. The roughly 20% difference between these values reflects that, in contrast with I_h ice, the surface of LDA ice is corrugated by thermal capillary waves, and hence it can accommodate noticeably more adsorbed molecules.

Interestingly, although the number of first layer molecules in systems IV and V is rather similar to each other (the difference being around 5–8%) for both ices, in the case of LDA the corresponding density peak is somewhat lower but broader in system V than in system IV. Further, the density peak of the first layer molecules occurs considerably closer to the ice phase in systems I and II on LDA, and in system I on I_h ice than at higher surface coverages. These findings suggest that the preferred orientation of the first layer molecules changes upon saturation of the adsorption monolayer, and further changes of this orientational preference might accompany the condensation of acetamide. This point is further addressed in the following sub-section.

4.2. Orientation of the first layer acetamide molecules

Since the orientation of a rigid molecule relative to an external plane can only be fully described by two independent orientational variables, such as the polar angles θ and ϕ of the surface normal vector in a local Cartesian frame fixed to the molecule, the full description of the orientational statistics requires the bivariate joint distribution of these variables [51,52]. Thus, in describing the orientational preferences of the first layer acetamide molecules relative to the ice surface, here we consider the interface normal vector oriented away from the ice phase, $\mathbf{X}$, and define the local frame in the following way. Its origin coincides with the position of the N atom, axis x points along the N–C bond, axis y still lies in the molecular plane, and axis z is the molecular normal. The axes of this frame are directed in such a way that the x and y coordinates

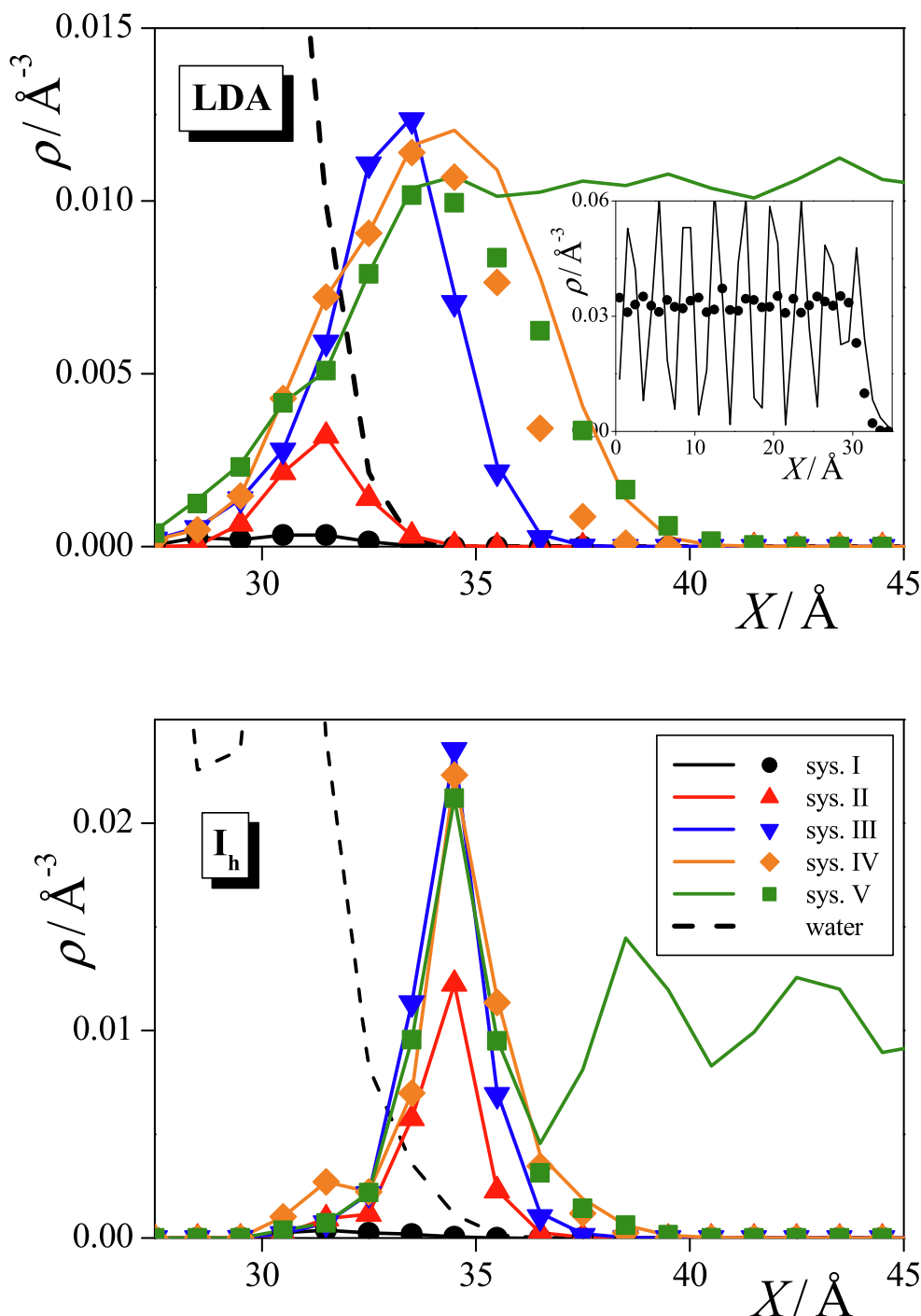


Fig. 4. Number density profiles of all acetamide molecules in the basic box (solid lines) and of the first layer ones (full symbols) along the surface normal axis, X , as obtained on LDA (top panel) and I_h (bottom panel) ices in systems I (black line, circles), II (red line, up triangles), III (blue line, down triangles), IV (orange line, diamonds), and V (green line, squares). The surface portion of the number density profile of the water molecules is also shown for reference (thick black dashed line). The inset shows the molecular number density profile of the water molecules in the LDA (filled circles) and I_h (solid line) ice phases at the lowest acetamide surface coverage considered (i.e., system I). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of the O atom are both positive, and the polar angle ϑ does not exceed 90° . Considering that while ϑ is an angle between two general spatial vectors (i.e., axis z of the local frame and $\mathbf{X}$), ϕ is formed by two vectors that are restricted, by definition, to lie in a given (i.e., the xy) plane, here we chose $\cos\vartheta$ and ϕ to be the orientational variables, as this way random orientation results in uniform bivariate distribution [51,52]. The definition of this local Cartesian frame and that of the polar angles ϑ and ϕ of the vector $\mathbf{X}$ in this frame are illustrated in Fig. 5.

The $P(\cos\vartheta, \phi)$ orientational maps of the first layer acetamide molecules are shown in Fig. 6 as obtained in systems I-V on both ices considered. As is seen, the obtained orientational distributions show the same features in both cases, with the only difference that their peaks are noticeably sharper in the case of crystalline than of LDA ice. In system I and, in the case of LDA ice, also in system II the orientational map exhibits a peak, marked here by A, close to the $\{\cos\vartheta = 1; \phi = 300^\circ\}$ point. A part of this peak occurs around the $\{\cos\vartheta = 1; \phi = 0^\circ\}$ point ($\phi = 0^\circ$ being equivalent with $\phi = 360^\circ$,

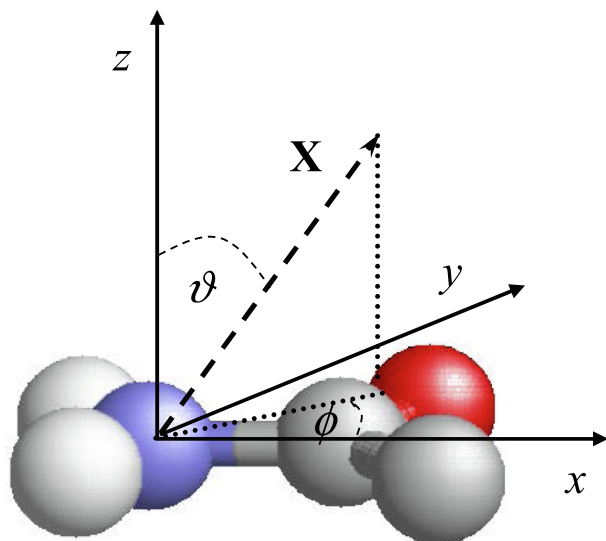


Fig. 5. Definition of the local Cartesian frame fixed to the individual acetamide molecules, and of the polar angles ϑ and ϕ describing the orientation of the molecule relative to the surface normal vector, pointing, by our convention, from the ice surface to the vapour phase, $\mathbf{X}$. The C, O, N and H atoms are represented by grey, red, blue and white spheres, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

see Fig. 5). It should be noted that in the case of $\cos\vartheta = 1$, (i.e., $\vartheta = 0^\circ$) the acetamide molecule lies in the plane of the ice surface, and hence the polar angle ϕ loses its meaning. In other words, all points of the map corresponding to $\cos\vartheta = 1$ are equivalent with each other. The fact that the peak of this orientational preference occurs around the ϕ value of 300° only reflects that when a molecule deviates somewhat from this preferred orientation, the deviation is preferentially such that the CH_3 group points as straight away from the ice phase as possible (within the constraint imposed by the value of $\cos\vartheta$), while one of the N–H bonds is tilted towards the ice phase and the other one is more or less parallel with the surface. The preferred orientation A together with this preferred deviation is illustrated at the bottom of Fig. 6.

Upon saturation of the first layer, the peak of the $P(\cos\vartheta, \phi)$ orientational map is shifted along the $\phi = 300^\circ$ line to $\cos\vartheta = 0$, reflecting, in accordance with the shift of the acetamide density peak (see Fig. 4), the change of the orientational preferences of the adsorbed acetamide molecules. In this orientation, marked here by B, the acetamide molecule stays perpendicular to the surface, pointing by the CH_3 group straight away from, and by one of the N–H bonds flatly towards the ice phase, while the other N–H bond is aligned nearly parallel with the ice surface. Finally, in system V (i.e., in the presence of condensed phase acetamide) a new orientational preference, marked here by C, occurs around the $\{\cos\vartheta = 0; \phi = 60^\circ\}$ point. In this orientation, being considerably stronger on I_h than on LDA ice, the plane of the acetamide molecule still stays perpendicular to the ice surface, however, now the CH_3 group

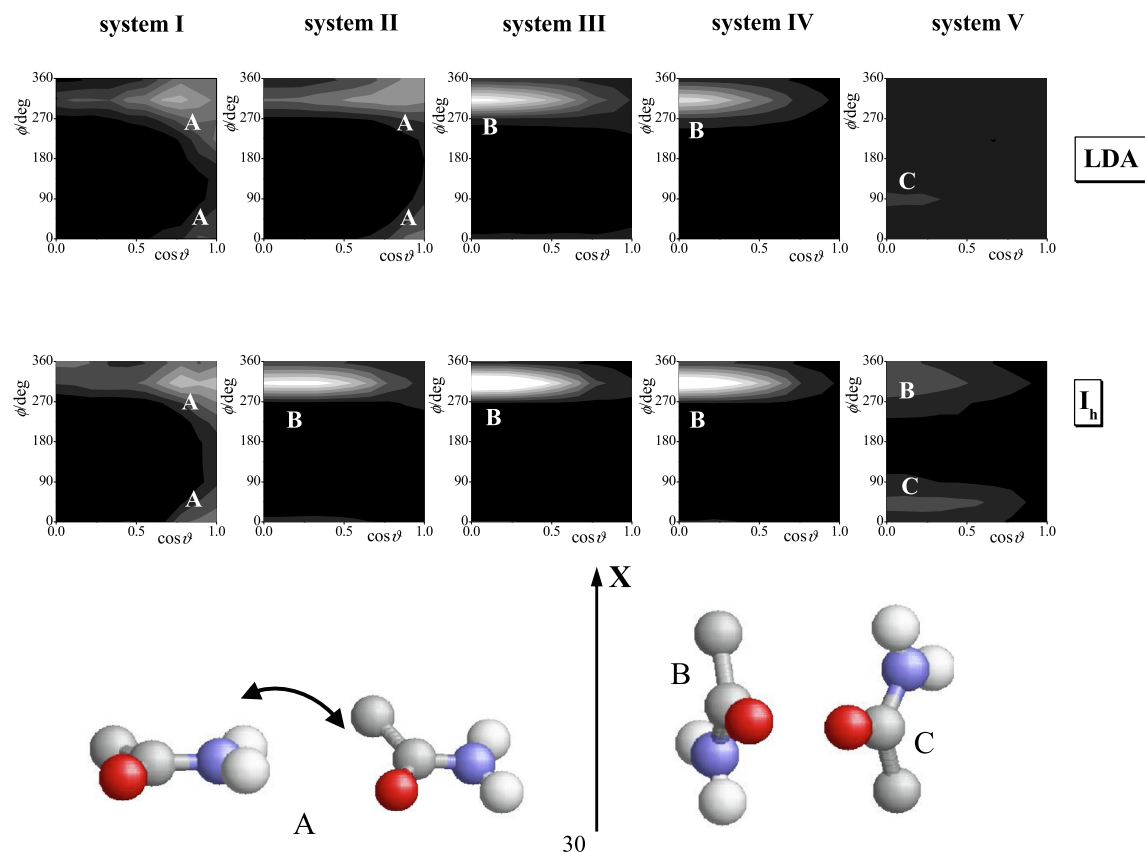


Fig. 6. Orientational maps of the first layer acetamide molecules, as obtained in systems I (left column), II (second column), III (middle column), IV (fourth column) and V (right column) on LDA (top row) and I_h (bottom row) ices. Lighter colours correspond to higher probabilities. The preferred orientations A, B and C are illustrated at the bottom of the figure. The C, O, N and H atoms are represented by grey, red, blue and white spheres, respectively; $\mathbf{X}$ is the surface normal vector pointing away from the ice phase. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

points straight towards the ice phase. Preferred orientations B and C are also illustrated at the bottom of Fig. 6. Besides orientation C, alignment B is also preferred at the surface of, at least, the I_h ice. It should be emphasized that the orientational preferences are much weaker in this system than what are observed below the point of condensation, indicating that here the first layer molecules can adopt any kind of alignment, presumably according to the orientations of the outer acetamide molecules.

To understand the physical background of these orientational preferences, it should be noted that at the surface of both ices considered the water molecules prefer, among others, orientations in which either an O–H bond points straight (i.e., perpendicularly to the surface plane), or at least one of the O–H bonds points flatly (i.e., tilting by about 20°–30° from the surface plane) away from the ice phase (see Fig. 7 of Ref. [23]). Thus, in orientation A both amide hydrogens can be donated, while the O atom can act as a H-acceptor in hydrogen bonds with surface water molecules of such alignments, as illustrated in Fig. 7.a. In orientation B, all these three groups can still be involved in H-bonds with the surface water molecules, however, due to steric reasons, the O atom and the N–H hydrogen being in *cis* position relative to it cannot form such H-bonds simultaneously. As a consequence, acetamide molecules of alignment B, unlike those of alignment A, can only form up to 2 hydrogen bonds with the surface waters, as illustrated in Fig. 7.b. On the other hand, an adsorbed acetamide molecule of alignment B occupies a considerably smaller surface area than that of alignment A. Thus, our results suggest that in the case of a highly unsaturated adsorption monolayer the adsorbed molecules try to maximize their H-bonding with the surface waters. Upon increasing saturation, their increasing competition for the surface and for these H-bonds triggers a change in their orientational preference, leading to the emergence of the preference for alignment B. This orientation can be further stabilised by the possible H-bond formation between the O atom of such an acetamide molecule with the N–H group laying almost parallel with the surface of its neighbour, being also in alignment B, as illustrated in Fig. 7.c.

In the case of condensed phase acetamide, surface molecules can easily replace any of their H-bonds with the surface waters by that with an outer layer acetamide molecule, which leads to the observed loss of marked orientational preferences even in the first molecular layer. Finally, the preference for alignment C can be explained by the fact that acetamides of this alignment can form two H-bonds with their neighbours of alignment B, in both of which the O atom is accepting the H atom of the tilted N–H bond of the other molecule. This possible double H-bond formation is also illustrated in Fig. 7.c.

4.3. Energetic background of the adsorption

To characterize the energetic background of the adsorption, we have calculated the distribution of the binding energy of the first layer acetamide molecules in systems I–V at both ices considered. The binding energy, U_b , is the energy required to move an adsorbed acetamide molecule to infinite distance from the system. In other words, U_b is the interaction energy of a given acetamide molecule with the rest of the system. Besides the distribution of U_b , we have also calculated the distributions of the U_b^{ice} and U_b^{lat} contributions to the binding energy, i.e., the interaction energy of the given acetamide molecule with the ice phase and with the other acetamide molecules in the system, respectively.

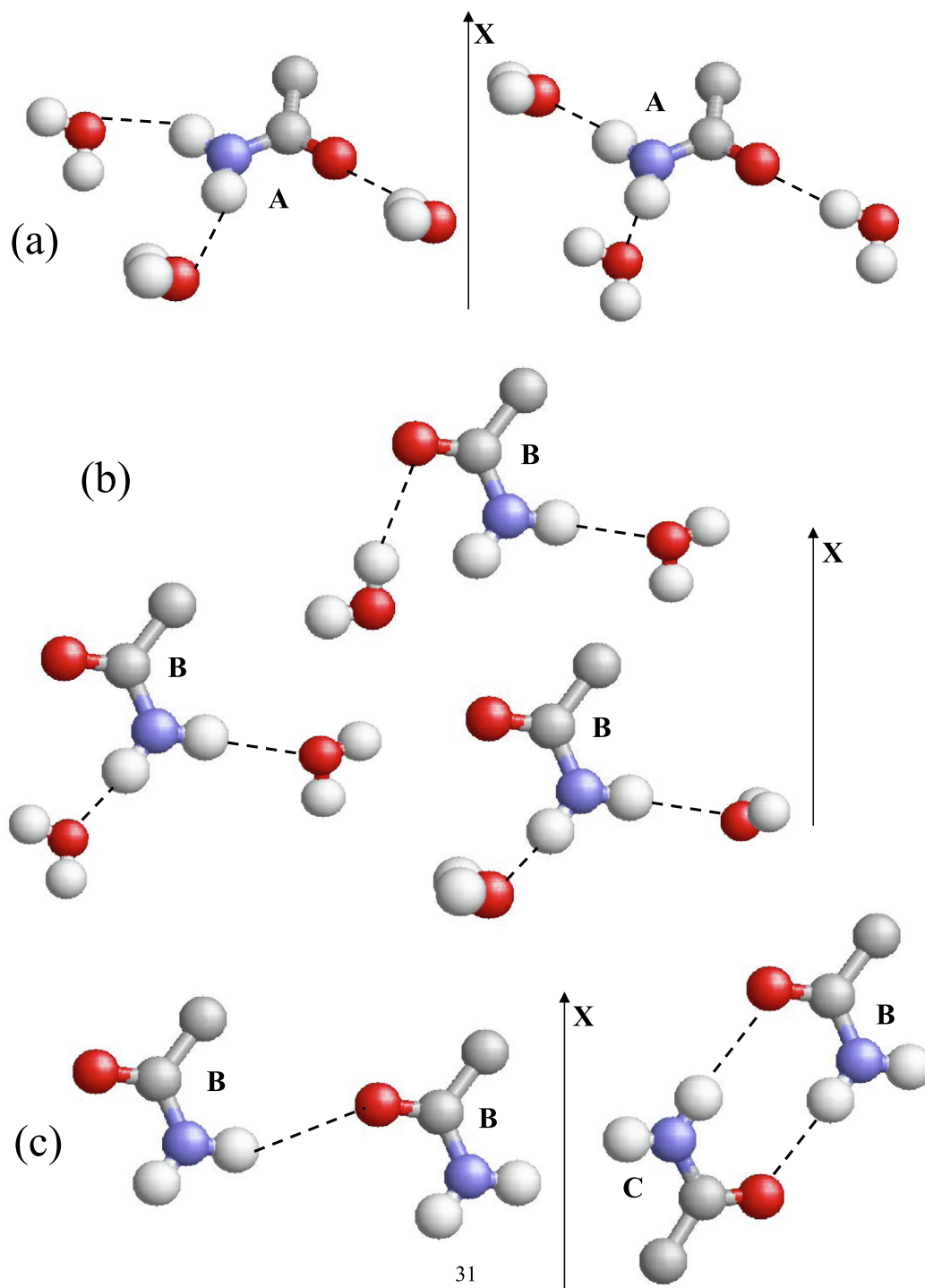
The $P(U_b)$, $P(U_b^{\text{ice}})$ and $P(U_b^{\text{lat}})$ distributions are shown in Fig. 8 as obtained on LDA (panel a) and I_h (panel b) ices. The distributions corresponding to the two different ice phases are rather similar to each other in almost every case. Thus, when the adsorption layer consists of only a few, more or less isolated acetamide molecules

(i.e., system I and, in the case of LDA ice, also system II) the $P(U_b^{\text{ice}})$ distribution exhibits its peak around –64 kJ/mol. Considering that the energy of a H-bond is about 20–25 kJ/mol, and that the H-bond between an acetamide NH_2 group and a water molecule is relatively weak [43], this finding suggests, in accordance with the observed orientational preferences, that adsorbed acetamide molecules typically form 3 H-bonds with the surface water molecules in these systems. To confirm this finding, we have also calculated directly the average number of H-bonded water neighbours of the adsorbed acetamide molecules in these systems (defining the H-bonds through the first minimum positions of the corresponding O–O_w or N–O_w and O–H_w or H–O_w radial distribution functions of 3.5 Å and 2.6 Å, respectively, where the subscript ‘w’ refers to the water molecule), and obtained the values of 2.85 and 2.80 for I_h and LDA ices, respectively. The mean value of $P(U_b^{\text{ice}})$ in system I can serve as a good estimate of the energy of adsorption at infinitely low surface coverage, a quantity that is experimentally also accessible. This value turns out to be –64.5 kJ/mol and –63.7 kJ/mol on LDA and I_h ices, respectively. We are not aware of any experimental study targeting this value; however, its measurement in the future would provide an additional important test of the validity of the present results. It should be noted that this value was earlier found to be –51.4 kJ/mol for acetone on I_h ice [28]; the 12.3 kJ/mol difference from the present value agrees excellently with the 10.6 kJ/mol difference between the hydration energies of acetone and acetamide [43].

In these systems of low surface coverage, the $P(U_b^{\text{lat}})$ distribution exhibits a huge and narrow peak at zero energy, reflecting the presence of adsorbed acetamide molecules that are isolated from each other. At the low energy side of this peak, a small second peak or shoulder appears around –20 – –18 kJ/mol. This minor peak is given by the few acetamide dimers that still occur at such low surface coverages, forming presumably one rather weak H-bond with each other. Due to the almost negligible lateral interactions, the distribution of the total binding energy, $P(U_b)$ turns out to be rather similar to $P(U_b^{\text{ice}})$ in these systems.

Upon increasing the surface coverage, the $P(U_b^{\text{ice}})$ distribution shifts to higher, while the $P(U_b^{\text{lat}})$ distribution shifts to lower energies, thus, the peak of both distribution occurs around –40 kJ/mol. This is the case when the adsorption monolayer is more or less saturated (i.e., system III on LDA, and systems III–IV on I_h ice), and even when it is still highly unsaturated, but the surface concentration is already large enough that the fraction of the isolated molecules vanishes (such as system II on I_h ice). This clear change of the shape and position of these distributions occurs simultaneously with the marked change in the orientational preferences of the acetamide molecules (from alignment A to B, see Fig. 6), discussed in the previous sub-section. In accordance with the aforementioned discussion, the roughly –40 kJ/mol energy suggests the formation of 2, relatively weak H-bonds of the acetamide molecules both with the surface waters and with each other. The fact that the interaction energy of the adsorbed acetamide molecules with each other is rather similar to that with the ice phase can explain the observed stability of the adsorption monolayer.

Finally, in the presence of condensed phase acetamide (i.e., system V), and even in that of at least a few outer layer acetamide molecules (i.e., system IV on LDA ice) the $P(U_b^{\text{ice}})$ distribution shifts to even higher energies, and splits to two peaks: one at –25 kJ/mol and another one around –5 – –3 kJ/mol. The first, main peak evidences the acetamide molecules that form one strong H-bond with the surface waters (involving, presumably, their O atom), while the second one (being only a shoulder in system IV on LDA ice) corresponds to those forming no H-bonds with the ice phase. This change of the $P(U_b^{\text{ice}})$ distribution occurs parallel with the emerge



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Fig. 7. Schematic illustration of the possible H-bond formation (a) between an acetamide molecule of alignment A and the surface water molecules, aligned in one of their preferred orientations, (b) between an acetamide molecule of alignment B and the surface water molecules, aligned in one of their preferred orientations, and (c) between two neighboring acetamide molecules in their preferred alignments B and C. The C, O, N and H atoms are represented by grey, red, blue and white spheres, respectively; **X** is the surface normal vector pointing away from the ice phase. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of the orientational preference for alignment C (Fig. 6), suggesting that this latter peak largely corresponds to acetamide molecules of this orientation. It should also be noted that the $P(U_b^{\text{ice}})$ distribution still exhibits a shoulder around -65 kJ/mol, indicating that a small fraction of the molecules still form 2 and even 3 H-bonds with the ice phase.

Due to the interaction with the outer layer acetamide molecules, the $P(U_b^{\text{lat}})$ distribution shifts further to negative energies. Its mean value turns out to be -63.8 kJ/mol on LDA and -62.1 kJ/mol on I_h ice, indicating the formation of 3 H-bonds with neighbouring acetamide molecules. While this distribution is rather symmetric on I_h ice, its peak occurs at considerably lower energies,

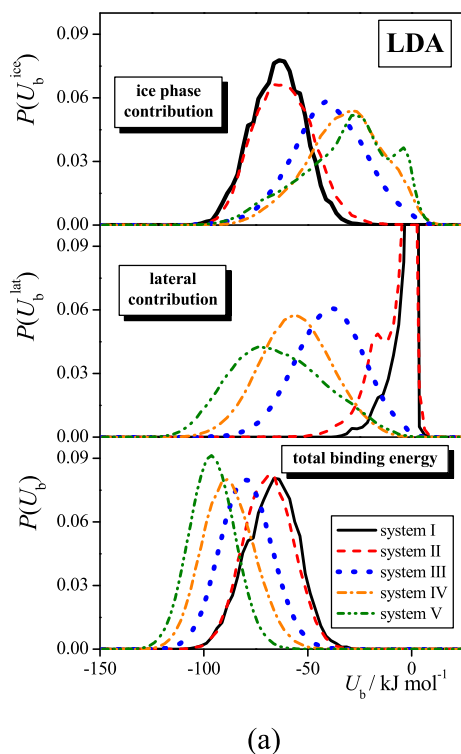


Fig. 8. Distribution of the binding energy of the first layer acetamide molecules (bottom panel) as well as that of its contributions coming from the other acetamide molecules in the system (middle panels) and from the ice phase (top panels), as obtained (a) on LDA and (b) on I_h ice in systems I (black solid lines), II (red dashed lines), III (blue dotted lines), IV (orange dash-dot lines), and V (green dash-dot-dot lines). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

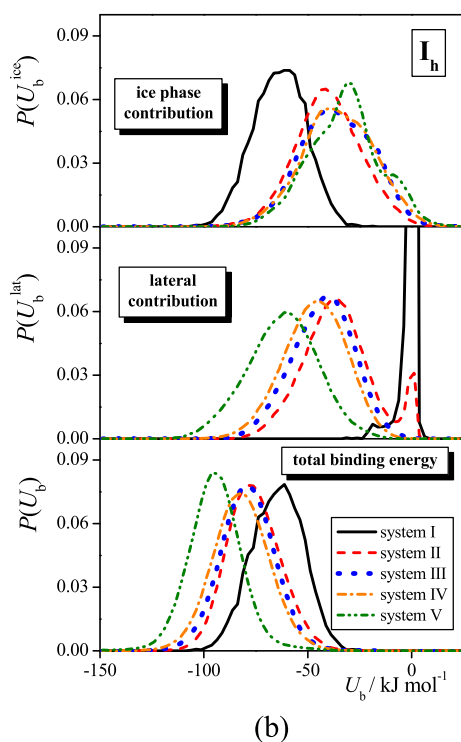


Fig. 8 (continued)

i.e., around -74 kJ/mol on LDA ice, suggesting that, in this latter case, a non-negligible fraction of the first layer molecules can form even 4 H-bonds with their acetamide neighbours.

Finally, the position of the peak of the $P(U_b)$ distribution shifts to progressively lower energies with increasing surface concentration, occurring around -65 kJ/mol in systems of isolated acetamide molecules, around -80 kJ/mol in systems of a more or less saturated monolayer, and around -95 kJ/mol in systems of condensed phase acetamide. Interestingly, the mean value of $P(U_b)$ agrees always very well with the sum of those of $P(U_b^ice)$ and $P(U_b^lat)$, the difference being within $1\text{--}2$ kJ/mol in every case. This finding is consistent with the above discussion that the adsorption is mostly governed by the formation of new H-bonds, and indicates that acetamide-water and acetamide-acetamide hydrogen bonds are of very similar strengths, and hence they are exchangeable for the adsorbed molecules with practically no energy cost. A similar behaviour was found earlier for the adsorption of HCN [29] and formamide [24].

5. Summary and conclusions

In this paper, we investigated in detail the adsorption of acetamide at the surface of both amorphous (LDA) and crystalline (I_h) ice at the tropospheric temperature of 200 K by GCMC computer simulations. The obtained results are consistent with the picture that acetamide, similarly to water, can form 4 H-bonds with its neighbours, 2 as a H-acceptor and 2 as a H-donor. This way, an adsorbed acetamide molecule can interact rather strongly both with the ice phase and with the rest of the adsorption layer. The adsorption is clearly governed by the possibility of new H-bond formation. Our results suggest that water-acetamide and acetamide-acetamide H-bonds are of rather similar energies, and hence water and acetamide neighbours of the acetamide molecules in the adsorption layer are exchangeable with each other as H-bonding partners for practically no energy cost. The strong lateral interaction between the adsorbed molecules gives rise to the markedly non-Langmuir shape of the adsorption isotherms. Further, the aforementioned equivalence of the water and acetamide neighbours as H-bonding partners, reflected also in the very similar binding energy contributions of the ice phase and the adsorption layer at monolayer coverage, results in the remarkable stability of the adsorption monolayer. The surface concentration of the saturated monolayer is estimated to be $10.2 \mu\text{mol}/\text{m}^2$ on LDA, and $8.1 \mu\text{mol}/\text{m}^2$ on I_h ice.

Due to this equivalence, acetamide molecules dissolved in the bulk ice phase can still form four H-bonds, now with the surrounding water molecules. Consequently, acetamide is found to be dissolved in both ice phases in a non-negligible concentration even at this low temperature. Although the data points of the dissolution isotherms are affected by rather large statistical noise, the shape of these isotherms is, at least, not incompatible with an exponential rise as a function of the chemical potential, suggesting that the dissolved molecules are still isolated from each other.

We found that, at low enough surface concentrations, the adsorbed acetamide molecules prefer to lay parallel with the ice surface, and if they deviate from this parallel alignment they preferentially point as straight away from the ice phase with their CH_3 group as possible. In this alignment, they can form 3 H-bonds with the surface water molecules. The energy of the adsorption at infinitely low surface coverage is estimated to be -64.5 kJ/mol and -63.7 kJ/mol at the surface of LDA and I_h ice, respectively. Any future experimental measurement of these quantities could provide an additional test of validity of our results. With increasing surface coverage, the interaction between the adsorbed molecules

becomes comparable with the adsorbate-adsorbent interaction, as acetamide molecules typically form 2 H-bonds with each other and another 2 with the surface waters. This change in the H-bonding pattern is accompanied by a marked change of the orientational preference: now the adsorbed molecules preferentially stay perpendicular to the surface, still pointing by the CH₃ group straight away from the ice phase. Finally, after the appearance of outer layer acetamide molecules (occurring right below the point of condensation on LDA ice, where traces of multilayer adsorption are clearly evidenced, and with the condensation on I_h ice), first layer molecules prefer to form 3 H-bonds with their acetamide neighbours and only 1 with the surface waters. Further, a small fraction of these molecules forms no H-bonds with the ice surface, at all. The appearance of such molecules is accompanied by the emerge of a new orientational preference, in which the apolar CH₃ group sticks straight towards the ice phase.

Because of the negligible photoactivity of acetamide, its major atmospheric sink is thought to be oxidation. Other scenarios concerning the atmospheric fate of acetamide, such as wet deposition are, however, also plausible. The results of the present simulations clearly support the importance of wet decomposition in this respect. The affinity of acetamide to water molecules may also indicate that acetamide can enhance the nucleation rate in the atmosphere, in accordance with the role amines are known to play in atmospheric nucleation [8].

CRedit authorship contribution statement

Mirjam Balbisi: Data curation, Formal analysis, Investigation, Software. **Réka A. Horváth:** Data curation, Investigation, Methodology, Software. **Milán Szőri:** Conceptualization, Funding acquisition, Project administration, Writing – original draft, Writing – review & editing. **Pál Jedlovsky:** Conceptualization, Funding acquisition, Data curation, Formal analysis, Methodology, Project administration, Resources, Supervision, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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