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ABSTRACT

The adsorption of acetamide on low density amorphous (LDA) ice is investigated by grand canonical Monte Carlo computer simulations at the temperatures 50, 100, and 200 K, characteristic of certain domains of the interstellar medium (ISM). We found that the relative importance of the acetamide–acetamide H-bonds with respect to the acetamide–water ones increases with decreasing temperature. Thus, with decreasing temperature, the existence of the stable monolayer, characterizing the adsorption at 200 K, is gradually replaced by the occurrence of marked multilayer adsorption, preceding even the saturation of the first layer at 50 K. While isolated acetamide molecules prefer to lay parallel to the ice surface to maximize their H-bonding with the surface water molecules, this orientational preference undergoes a marked change upon saturation of the first layer due to increasing competition of the adsorbed molecules for H-bonds with water and to the possibility of their H-bond formation with each other. As a result, molecules stay preferentially perpendicular to the ice surface in the saturated monolayer. The chemical potential value corresponding to the point of condensation is found to decrease linearly with increasing temperature. We provide, in analogy with the Clausius–Clapeyron equation, a thermodynamic explanation of this behavior and estimate the molar entropy of condensed phase acetamide to be 34.0 J/mol K. For the surface concentration of the saturated monolayer, we obtain the value $9.1 \pm 0.8 \mu\text{mol/m}^2$, while the heat of adsorption at infinitely low surface coverage is estimated to be $-67.8 \pm 3.0 \text{ kJ/mol}$. Our results indicate that the interstellar formation of peptide chains through acetamide molecules, occurring at the surface of LDA ice, might well be a plausible process in the cold (i.e., below 50 K) domains of the ISM; however, it is a rather unlikely scenario in its higher temperature (i.e., 100–200 K) domains.

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I. INTRODUCTION

The interstellar presence of prebiotic molecules suggests that their extraterrestrial origin on Earth can be plausible.^{1,2} Ribose, a building block of RNA that could have both stored information and catalyzed reactions in primitive life, has recently been identified in primitive meteorites.³ Furthermore, meteorites also contain several organic compounds that are essential for life. Among these molecules, acetamide, the largest peptide detected in interstellar space so far,⁴ has been identified in the environments of Sagittarius

B2 (Sgr B2)⁴ and Orion Kleinman-Low Nebula,⁵ as well as in comets,⁶ and it has been suggested to be a source of larger molecules consisting of a peptide bond under such extreme conditions.⁵ The origin of acetamide in the interstellar medium (ISM) is still under debate, although, on the basis of *ab initio* calculations, Foo *et al.*⁷ and Kothari *et al.*⁸ proposed bimolecular gas-phase reaction mechanisms toward the acetamide formation in the ISM. On the other hand, Quan and Herbst concluded that most organic species in Sgr B2(N) are formed on grain surfaces.⁹ Acetamide has also been produced in various model ice experiments,^{10,11} indicating that it could

be formed on the ice mantles of interstellar grains as well. At conditions relevant to the ISM (i.e., 10–100 K), the surface of the cold dust grains is mainly composed of low density amorphous (LDA) water ice.¹² Furthermore, Garrod *et al.* stated that if acetamide is formed by the addition of grain-surface CH_3 to HNCO , followed by hydrogenation, then the established model can well reproduce the abundance of acetamide.¹³ Thus, acetamide molecules can be desorbed from the grain surface, making the liberated acetamide detectable with a 100 m Green Bank Telescope (GBT) by means of rotational transitions.⁴ The total column density for acetamide toward Sgr B2(North core, Large Molecule Heimat) is estimated to vary between 4.34×10^{13} and $2.27 \times 10^{14} \text{ cm}^{-2}$,⁴ which can be converted into a local concentration of $2.4\text{--}12.6 \times 10^{-25} \text{ mol/dm}^3$, assuming the average H_2 column density $[\text{N}(\text{H}_2)]$ of $3 \times 10^{24} \text{ cm}^{-2}$, which corresponds to the H_2 density of 10^7 cm^{-3} .¹⁴

Although reactions involving molecules with an amide functional group offer alternative pathways to the formation of peptide chains,¹⁰ the low relative abundance of acetamide itself cannot be sufficient for that. Icy surfaces can, however, provide an excellent place for such aggregation to occur due to the presence of both hydrogen bond donor and acceptor groups in the acetamide structure and also due to the large permanent electric dipole moment of the acetamide molecule of 3.8 D.¹⁵ Therefore, by testing the plausibility of the amide-based formation pathway of peptides in the ISM, the adsorption of small amides, such as acetamide, on LDA ice at temperatures characteristic to the ISM has to be characterized. Unfortunately, we are not aware of any experimental study in this respect.

Computer simulation investigations can provide a viable alternative to experimental studies since in a computer simulation, such a deep, molecular level insight can be gained into a suitable chosen model of the system of interest that can hardly be provided by any experiment.¹⁶ Among the various computer simulation methods, grand canonical Monte Carlo (GCMC) simulations^{16,17} are particularly suitable to study adsorption processes. Namely, in GCMC, the chemical potential rather than the number of the particles of a given type is fixed during the simulation.^{16,17} Thus, by performing a set of GCMC simulations, in which the chemical potential of the adsorbate is systematically varied, the adsorption isotherm can readily be calculated. The GCMC method has, indeed, successfully been used in the past one and half decades to simulate the adsorption of a number of small molecules at the surface of both LDA^{18–22} and crystalline ices^{19,23–30} and on other adsorbents, such as various carbonaceous materials,^{31–33} self-assembled monolayers,^{34,35} metal oxides,^{36–38} or covalent organic frameworks,^{39,40} and also inside clathrate hydrates,^{41–44} zeolites,^{45,46} clay minerals,^{47,48} or protein crystals.⁴⁹ However, the adsorption of amides on icy surfaces has, until recently, not been addressed by computer simulation methods, either.

A few years ago, we reported a GCMC investigation of the adsorption of formamide, the smallest molecule that contains a peptide bond, at icy surfaces at temperatures relevant to the ISM.¹⁹ In accordance with the general notion that the mixing of formamide and water is nearly ideal,^{50–52} we observed a strong multilayer adsorption of formamide on LDA ice, occurring even before the first adlayer gets saturated. Very recently, we also studied the adsorption of acetamide on LDA and crystalline (I_h) ices, however, under conditions (i.e., at 200 K) that are characteristic to the upper troposphere

of Earth rather than to the ISM.⁵³ In contrast with formamide, the adsorption monolayer was found to be remarkably stable here, and only traces of multilayer adsorption were evidenced immediately before the condensation of acetamide. Furthermore, besides adsorption, non-negligible dissolution of acetamide into the bulk ice phase was also observed.

In this paper, we extend this study to temperatures characteristic to the interstellar medium. The main question we aim at addressing here is how the adsorption and dissolution of acetamide change with the decreasing temperature and, eventually, whether the accumulation of acetamide either at the surface or inside interstellar ice is a plausible process.

The remainder of this paper is organized as follows. In Sec. II, details of the calculations performed are given. The obtained results concerning the adsorption isotherm and the properties of the adsorption layer are discussed in detail in Secs. III and IV, respectively. Finally, in Sec. V, the main conclusions of this study are summarized.

II. COMPUTATIONAL DETAILS

The adsorption of acetamide at the surface of LDA ice has been investigated by performing three sets of Monte Carlo simulations on the grand canonical (μ , V , T) ensemble at the respective temperatures (T) of 50, 100, and 200 K. The two lower temperatures are characteristic of typical domains of the ISM. Although in certain parts of the ISM the temperature might even reach 200 K, this temperature is much less characteristic to the interstellar environment; we include these data for providing a broader range in which the

TABLE I. Data of the adsorption isotherm of acetamide on LDA ice, as obtained at 50 K.

μ (kJ mol ⁻¹)	$\langle N_{\text{ads}} \rangle$	p/p_0	Γ ($\mu\text{mol m}^{-2}$)
−56.23	0.1815	4.66×10^{-15}	1.08×10^{-2}
−55.19	0.5010	5.68×10^{-14}	2.98×10^{-2}
−54.15	4.017	6.91×10^{-13}	0.239
−52.07 ^a	4.829	1.03×10^{-10}	0.287
−51.03	13.11	1.25×10^{-9}	0.779
−49.99	24.38	1.52×10^{-8}	1.45
−48.95	36.78	1.86×10^{-7}	2.19
−47.91	40.76	2.26×10^{-6}	2.42
−46.87 ^b	56.84	2.75×10^{-5}	3.38
−45.83	97.34	3.35×10^{-4}	5.78
−44.79 ^c	134.8	4.09×10^{-3}	8.01
−43.75	165.1	4.98×10^{-2}	9.81
−42.71 ^d	215.7	0.607	12.8
−42.30	595.5		
−41.68 ^e	594.3		
−40.64	595.0		
−39.60	593.9		

^aState I.

^bState II.

^cState III.

^dState IV.

^eState V.

temperature dependence of the adsorption is addressed and also for reference purposes. The rectangular basic simulation box has always consisted of 2880 water molecules; the lengths of its X , Y , and Z edges have been 100, 35.926, and 38.891 Å, respectively, with X being the axis perpendicular to the ice surface. The chemical potential of acetamide, μ , has been varied in every set of simulations from values corresponding to practically no acetamide molecules in the basic box to those corresponding to the condensed phase of acetamide. The μ values at which the simulations have been performed at 50, 100, and 200 K are collected in Tables I–III, respectively.

As in our previous study,⁵³ acetamide and water molecules have been described by the rigid OPLS⁵⁴ and TIP4P⁵⁵ potential models, respectively, which supposed to be compatible with each other.⁵⁴ This model combination was shown to well reproduce several thermodynamic, structural, and dynamical properties of the system^{54,56} and was successfully applied to calculate the hydration free energy difference between acetamide and acetone and urea.⁵⁷ Both models are pairwise additive; thus, the potential energy of the system is calculated as the sum of the Lennard-Jones and charge–charge Coulomb contributions of all pairs of interaction sites of all molecule pairs. The interaction parameters of these models are summarized in Table IV. The lengths of the C=O, C–CH₃, C–N, and N–H bonds of the acetamide molecule are 1.248, 1.507, 1.380, and 0.990 Å, respectively, while its O=C–C, O=C–N, and H–N–H bond angles are 121.4°, 119.3°, and 120.2°, respectively. The atoms are arranged in a planar way, with the CH₃ group being treated as a united atom.⁵⁴

TABLE II. Data of the adsorption isotherm of acetamide on LDA ice, as obtained at 100 K.

μ (kJ mol ^{−1})	$\langle N_{\text{ads}} \rangle$	p/p_0	$\Gamma/(\mu\text{mol m}^{-2})$
−58.44	0.1017	3.94×10^{-8}	6.04×10^{-3}
−56.78	0.3160	2.91×10^{-7}	1.88×10^{-2}
−55.95	0.4502	7.91×10^{-7}	2.68×10^{-2}
−54.29	1.195	5.84×10^{-6}	7.10×10^{-2}
−53.45	1.570	1.59×10^{-5}	9.33×10^{-2}
−52.62 ^a	3.022	4.32×10^{-5}	0.180
−51.79	10.22	1.17×10^{-4}	0.607
−50.96	19.11	3.19×10^{-4}	1.20
−50.13	22.06	8.67×10^{-4}	1.31
−49.30	34.06	2.36×10^{-3}	2.08
−48.47	41.86	6.41×10^{-3}	2.49
−47.63 ^b	64.33	1.74×10^{-2}	3.88
−46.80	121.7	4.74×10^{-2}	7.23
−45.97 ^c	134.6	0.129	8.06
−45.14	207.3	0.350	12.3
−44.31 ^d	297.9	0.951	17.8
−44.23	585.0		
−43.89	588.7		
−43.48 ^e	586.2		
−42.65	589.0		

^aState I.

^bState II.

^cState III.

^dState IV.

^eState V.

TABLE III. Data of the adsorption isotherm of acetamide on LDA ice, as obtained at 200 K.

μ (kJ mol ^{−1})	$\langle N_{\text{ads}} \rangle$	p/p_0	$\Gamma/(\mu\text{mol m}^{-2})$
−64.57	0.0035	3.72×10^{-5}	2.08×10^{-4}
−62.08	0.0107	1.67×10^{-4}	6.36×10^{-4}
−59.58	0.0503	7.47×10^{-4}	2.99×10^{-3}
−57.92	0.1398	2.03×10^{-3}	8.31×10^{-3}
−56.26	0.2749	5.52×10^{-3}	1.63×10^{-2}
−54.60	0.8425	1.50×10^{-2}	5.01×10^{-2}
−53.76	1.591	2.47×10^{-2}	9.46×10^{-2}
−52.93 ^a	1.339	4.08×10^{-2}	0.138
−52.10	6.002	6.72×10^{-2}	0.357
−51.27	10.09	0.111	0.612
−50.44	24.95	0.183	1.61
−49.61 ^b	52.30	0.301	3.15
−49.11	120.1	0.407	7.20
−48.78 ^c	127.5	0.497	7.68
−48.44	138.5	0.607	8.53
−48.11	148.5	0.741	9.00
−47.78 ^d	175.2	0.905	10.5
−47.45 ^e	552.0		
−46.28	567.7		
−45.45	562.5		

^aState I.

^bState II.

^cState III.

^dState IV.

^eState V.

In the water model, the O–H bond length and H–O–H bond angle are 0.9572 Å and 104.52°, respectively, while the negative fractional charge is displaced by 0.1577 Å from the O atom along the bisector of the H–O–H angle.⁵⁵ According to the original parameterization of these models,^{54,55} all interaction has been truncated to zero beyond the center–center cut-off distance of 12.5 Å.

The simulations have been performed by the program MMC.⁵⁸ In the simulations, insertion/deletion and particle displacement moves have been attempted in alternating order. Insertion and deletion attempts have been done with equal probabilities. In these moves, either a randomly chosen acetamide molecule was tried to

TABLE IV. Interaction parameters of the molecular models used.

Molecule	Site	q (e)	σ (Å)	ϵ (kJ mol ^{−1})
Acetamide	C	0.380	3.750	0.440
	O	−0.380	2.960	0.879
	CH ₃	0.000	3.910	0.670
	N	−0.666	3.250	0.712
	H	0.333	...	...
Water	O	0.000	3.154	0.649
	H	0.520	...	...
	M ^a	−1.040	...	...

^aNon-atomic site, located along the bisector of the H–O–H angle.

be taken away from the system or a new acetamide molecule was tried to be inserted in the basic box. These moves have been performed according to the cavity biased scheme of Mezei,^{59,60} i.e., insertions have only been attempted into pre-existing empty cavities of the radius of at least 2.5 Å. Trial moves have been accepted

or rejected according to this scheme.^{59,60} In a particle displacement attempt, a randomly chosen molecule of either type has been randomly displaced within 0.25 Å and rotated around a randomly chosen space-fixed axis by a random angle not exceeding 15°. These moves have been accepted or rejected according to the standard Metropolis criterion.^{16,61} Insertion/deletion and particle displacement attempts have typically been accepted with probabilities of at least 0.0001% and 5%, respectively.

The LDA ice phase, being in the middle of the basic box along its axis *X*, has been prepared, as described in our previous paper, by thermalizing the *I_h* phase of ice in 10⁸, 2 × 10⁸, and 10⁸ Monte Carlo step long trajectories at 300, 350, and again at 300 K, respectively, followed by its quenching in another 10⁸ step long trajectory at 200 K.⁵³ The starting configuration of the simulations has, then, been obtained by randomly placing an acetamide molecule in the vapor phase. The systems have been equilibrated by performing 5 × 10⁹–3 × 10¹⁰ Monte Carlo steps until both the number of acetamide molecules and the energy of the system were fluctuating around their equilibrium values. Then, the mean number of the acetamide molecules present in the basic box, $\langle N \rangle$, has been averaged over a 2 × 10⁹ Monte Carlo step long trajectory. Equilibrium snapshots of selected systems, simulated at 100 K, are shown in Fig. 1 both from top and side views.

The average number of acetamide molecules that are dissolved in the bulk ice phase has been calculated in 1000 sample configurations, separated from each other by 10⁶ Monte Carlo step long trajectories. For this purpose and to also identify the acetamide molecules forming the first layer at the ice surface, a two-step identification of the truly interfacial molecules (ITIM) analysis⁶² has been performed, as described in our previous papers,^{18,53} using a probe sphere radius of 2 Å and a grid spacing of 0.5 Å. Thus, in the first step, the water molecules forming the two surface layers of the LDA phase have been determined; all acetamide molecules located between these two layers of water have, then, been considered as being dissolved in the ice phase and have been neglected in the next step. In the second step, the acetamide molecules forming the first molecular layer at the ice surface (i.e., those being in direct contact with the LDA phase) have been determined.^{18,53} Finally, at selected chemical potential values (shown in Tables I–III), 2500 sample configurations, separated from each other by 10⁶ Monte Carlo step long trajectories, have been dumped. All properties calculated have been averaged not only over these sample configurations but also over the two ice surfaces present in the basic box.

III. ADSORPTION ISOTHERMS

The average number of adsorbed acetamide molecules, $\langle N_{\text{ads}} \rangle$, is plotted as a function of the acetamide chemical potential, μ , in Fig. 2 as obtained from the simulations at 50, 100, and 200 K. The corresponding data are also included in Tables I–III. Since practically no acetamide molecule has been found in the bulk vapor phase in any case, $\langle N_{\text{ads}} \rangle$ has simply been calculated by subtracting the average number of acetamide molecules dissolved in the bulk LDA phase from that of all acetamide molecules in the basic box. It should be noted that while at 200 K the number of dissolved molecules is found to increase exponentially with μ ,⁵³ at the two lower temperatures, the number of dissolved acetamide molecules has never exceeded 1. This finding indicates that, in a clear contrast with their

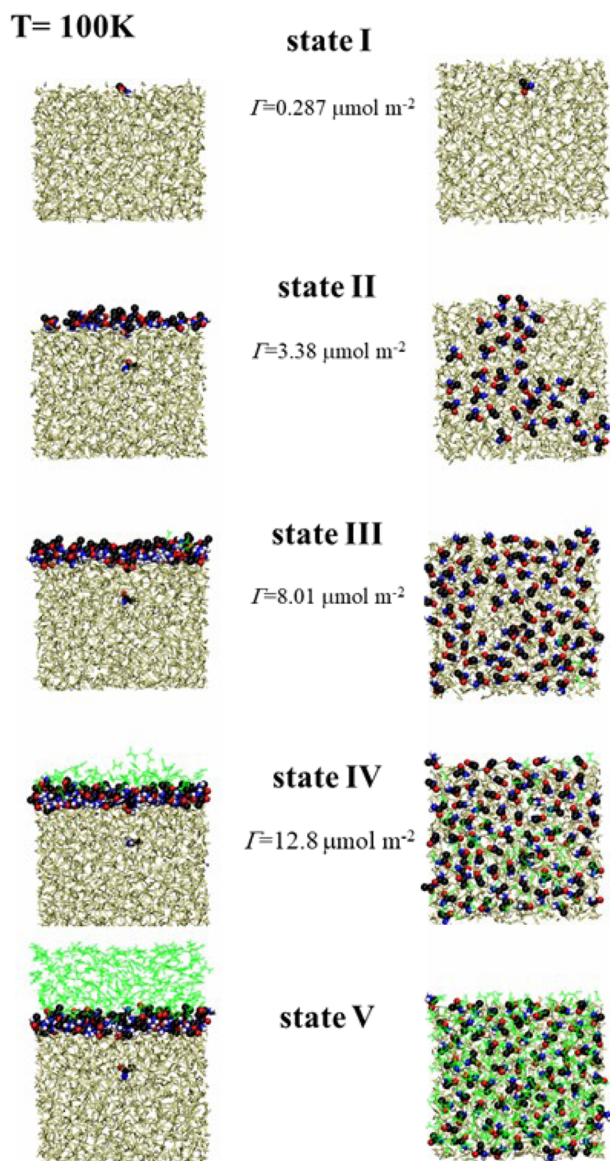


FIG. 1. Surface portion of equilibrium snapshots of the system simulated at 100 K in states I (top row), II (second row), III (third row), IV (fourth row), and V (bottom row), shown in both side (left) and top (right) views. Water molecules are shown by yellow sticks; acetamide molecules belonging to the first molecular layer and those dissolved in the LDA phase are shown in the ball and stick representation using the color code that the C atoms and CH₃ groups are marked by black, while the N, O, and H atoms are represented by blue, red, and white balls, respectively. Outer layer acetamide molecules are shown by green sticks.

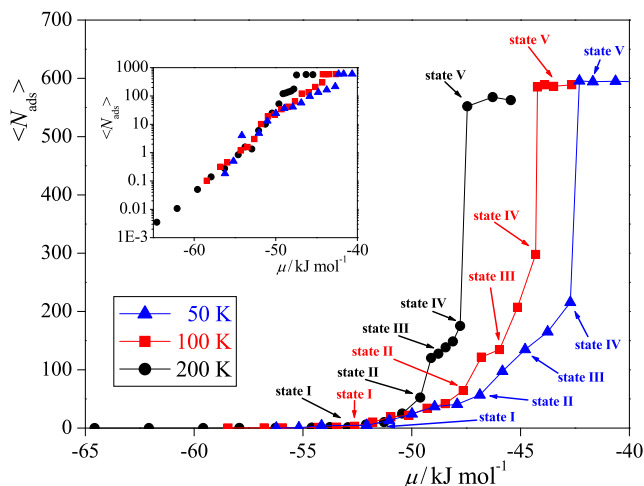


FIG. 2. Adsorption isotherm of acetamide on LDA ice, shown in the $\langle N_{\text{ads}} \rangle$ vs μ form, as obtained at 50 K (blue triangles), 100 K (red squares), and 200 K (black circles) from the simulations. The lines connecting the points are just guides to the eye. The inset shows the same data on a logarithmic scale. The systems chosen for detailed analysis at each temperature are indicated by the arrows.

adsorption (which must be exothermic due to the decrease of the entropy accompanying the accommodation of vapor phase particles at the ice surface^{63,64}), the dissolution of the acetamide molecules in the LDA phase is an endothermic process, as it becomes more pronounced with the increasing temperature. Since the dissolution of acetamide molecules in the LDA phase implies the replacement of some water–water H-bonds with acetamide–water ones, this finding suggests, in accordance with earlier results,⁵⁷ that acetamide–water H-bonds are relatively weak, certainly weaker than the water–water ones.

The obtained adsorption isotherms exhibit an exponential increase at low chemical potential values (as illustrated by the inset of Fig. 2, showing the same isotherms on a logarithmic scale), followed by a plateau of relatively low steepness in the chemical potential range of about -49.0 to -47.5 kJ/mol at 200 K. This plateau, assumed to correspond to the presence of the more or less saturated adsorption monolayer, occurs in a considerably narrower μ range (around -46.5 kJ/mol) at 100 K and disappears completely at 50 K. The $\langle N_{\text{ads}} \rangle$ value of the plateau of about 130 provides a rough estimate for the number of acetamide molecules corresponding to the saturated adsorption monolayer. At 100 K, the plateau is followed by another steeply rising part of the isotherm, evidencing multilayer adsorption. Similar behavior is seen at 50 K above the $\langle N_{\text{ads}} \rangle \approx 130$ value, while at 200 K, only traces of multilayer adsorption are seen. Finally, at a certain μ value, the isotherms exhibit a sharp jump, corresponding to the condensation of acetamide, above which the basic box is filled with acetamide molecules.

The acetamide chemical potential values corresponding to the point of condensation, μ_0 , are plotted against the temperature in Fig. 3. As is seen, μ_0 decreases linearly with the increasing temperature. Similar behavior was earlier observed for a number of small molecules.^{18–22,43} This linear behavior can be understood considering the following derivation, done in analogy with that of the

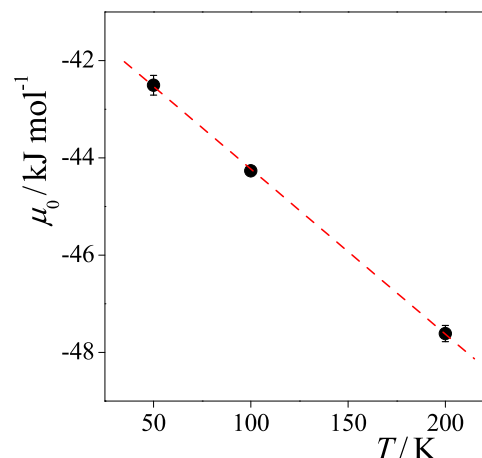


FIG. 3. Temperature dependence of the chemical potential corresponding to the point of condensation. The data obtained from the simulations and the straight line fitted to them are shown by black circles and red dashed line, respectively. Error bars are shown when larger than the symbols.

Clausius–Clapeyron equation.⁶⁴ Using the Gibbs–Duhem relation, the infinitesimal change of the pressure, dp , can be expressed as

$$dp = \rho_S dT + \rho_N d\mu, \quad (1)$$

where $\rho_S = S/V$ and $\rho_N = N/V$ are the entropy density and number density, respectively, of the system. For states laying along the coexistence line between phases I and II, the pressure in the two coexisting phases, p^I and p^{II} , respectively, is equal to each other. Thus, if the infinitesimal change, accompanied by dp , keeps the system being along the coexistence line, the pressure changes should also be equal in the two phases, i.e.,

$$dp^I = dp^{II}. \quad (2)$$

Substituting Eq. (1) into (2), one gets

$$\rho_S^I dT + \rho_N^I d\mu = \rho_S^{II} dT + \rho_N^{II} d\mu, \quad (3)$$

and hence,

$$\frac{d\mu}{dT} = -\frac{\rho_S^I - \rho_S^{II}}{\rho_N^I - \rho_N^{II}}. \quad (4)$$

Equation (4) represents the equivalent of the Clapeyron equation, being valid for all phase coexistences. Assuming now that phase I is much denser than phase II, i.e., $\rho_N^I \gg \rho_N^{II}$ and, hence, $\rho_S^I \gg \rho_S^{II}$, Eq. (4) can be simplified to

$$\frac{d\mu}{dT} = -\frac{\rho_S^I}{\rho_N^I} = -\frac{S^I/V^I}{N^I/V^I} = -\frac{S^I}{N^I} = -S_m^I, \quad (5)$$

where S_m^I denotes the molar entropy of dense phase I. Since the molar entropy of a dense, cold phase is not expected to noticeably depend on the temperature, μ_0 should, indeed, decrease linearly with the temperature, in accordance with our present and earlier^{18–22,43}

results. In the case of acetamide, this molar entropy is estimated here to be 34.0 J/mol K.

To further analyze the obtained adsorption isotherms, we have converted them to the more conventional Γ vs p_{rel} form, where $p_{\text{rel}} = p/p_0$ is the relative pressure (i.e., the pressure, p , normalized by that of the saturated vapor of acetamide, p_0) and Γ is the surface concentration of acetamide. The $\Gamma(p_{\text{rel}})$ isotherms have been calculated as

$$\Gamma = \frac{\langle N_{\text{ads}} \rangle}{2YZ} \quad (6)$$

(where the factor of 2 in the denominator accounts for the two LDA surfaces present in the basic box) and³⁷

$$p_{\text{rel}} = \frac{p}{p_0} = \frac{\exp(\mu/k_B T)}{\exp(\mu_0/k_B T)}. \quad (7)$$

It should be noted that since p_{rel} is the relative pressure of the vapor phase with respect to the saturated vapor, values of p_{rel} above 1 are of no physical meaning, and hence, we have only converted the $\langle N_{\text{ads}} \rangle$ vs μ data to the $\Gamma(p_{\text{rel}})$ isotherm up to the p_{rel} value of 1.

The obtained $\Gamma(p_{\text{rel}})$ isotherms are plotted in Fig. 4, while the corresponding data are also included in Tables I–III. As is seen, the shape of the obtained isotherms is markedly different from that of the Langmuir isotherm. This may not be obvious at the first sight for the 50 K data; however, fitting the Langmuir isotherm to the simulation results was not successful even at this temperature. Since the approximation of the Langmuir isotherm is based on the neglect of the lateral (i.e., adsorbate–adsorbate) interaction,^{63,64} the clearly non-Langmuir character of the obtained isotherms indicates the importance of the interaction between the acetamide molecules within the adsorption layer. This is not surprising, considering that an acetamide molecule can form up to four H-bonds with its acetamide neighbors. This point is further addressed in Secs. IV B and IV C.

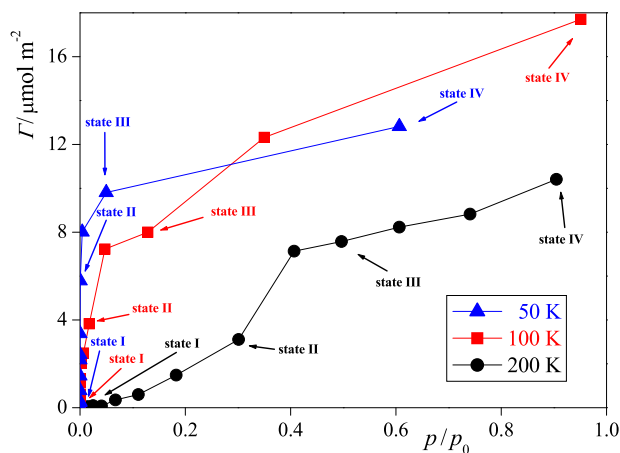


FIG. 4. Adsorption isotherm of acetamide on LDA ice, shown in the Γ vs p_{rel} form, as obtained at 50 K (blue triangles), 100 K (red squares), and 200 K (black circles) from the simulations. The lines connecting the points are just guides to the eye. The systems chosen for detailed analysis at each temperature are indicated by the arrows.

Having no access to the pressure of vapor phase acetamide from the simulations (as practically no acetamide molecule occurs in the vapor phase in any case), it is rather difficult to address the question whether the obtained isotherms are compatible with non-negligible acetamide adsorption on LDA surfaces under interstellar conditions. The pressure of the saturated acetamide vapor, p_0 , can be estimated by using the following Antoine equation:⁶⁵

$$\log_{10} p_0 = A - \frac{B}{T + C}, \quad (8)$$

where the values of the Antoine parameters for acetamide are $A = 10.94163$, $B = 4066.340$ K, and $C = 0.077$ K⁶⁶ and the value of p_0 is in kPa units. However, these parameters are only assumed to provide a good estimate of p_0 in the temperature range of 271–300 K,⁶⁶ well above the temperatures considered here. This equation yields the p_0 value of 8.7×10^{-2} Pa at 271 K, which can, thus, be regarded as a (very crude) upper estimate of p_0 at lower temperatures. Using this value for p_0 and assuming the acetamide vapor to be an ideal gas, the surface density value of about $0.1 \mu\text{mol}/\text{m}^2$ corresponds to the vapor phase acetamide concentrations of about 10^5 , 10^{12} , and 10^{15} molecules/ dm^3 at 50, 100, and 200 K, respectively. It has to be emphasized, however, that these values are very crude (i.e., by several orders of magnitude too high) upper estimates of the real acetamide concentrations required for such adsorption, getting progressively worse with the decreasing temperature. Thus, the error of this estimate of the acetamide concentration required for non-negligible adsorption might well cover the roughly 5 orders of magnitude difference between this value and the acetamide concentration in the ISM, estimated to be 1 molecules/ dm^3 ,⁴ at 50 K. On the other hand, it seems to be rather unlikely that the 12 and 15 orders of magnitude differences, obtained at 100 and 200 K, respectively, can fully be accounted for by the use of the p_0 value corresponding to 271 K. In other words, our results suggest (but by no means prove) that non-negligible acetamide adsorption might well occur on LDA surfaces at the low enough temperature (i.e., 50 K and below) domains of the ISM, but it cannot be expected in the domains of high (i.e., 100–200 K) temperature.

IV. CHARACTERIZATION OF THE ADSORPTION LAYER

To investigate the structural and energetic properties of the adsorption layer in detail, we have collected sample configurations at five selected chemical potential values at each temperature and performed detailed analyses of these systems. The states considered in the detailed analyses have been chosen in the following way. At each temperature, state I corresponds to the situation when the adsorbed acetamide molecules are largely separated from each other; states II and III correspond to a largely unsaturated monolayer and a more or less saturated adsorption monolayer, respectively, while state IV, chosen to be right below the point of condensation, corresponds to multilayer adsorption. Finally, for reference purposes, a chemical potential value corresponding to the condensed phase of acetamide (state V) has also been chosen. The μ values corresponding to states I–V are indicated in Tables I–III, and the data points corresponding to them are also marked in Figs. 2 and 4.

A. Density profiles

The molecular number density profiles of all acetamide molecules in the system and of those forming the first molecular layer at the LDA surface are shown in Fig. 5, as obtained in states I–V at the three temperatures considered. For reference, the outmost portion of the number density profile of the water molecules forming the LDA phase is also shown.

As is seen, the profile of all molecules always coincides with that of the first layer ones in states I and II and also in state III at the two higher temperatures. In these systems, the adsorption is thus, indeed, strictly monomolecular. In state IV, however, the density of the first layer molecules is considerably narrower than that of all molecules, indicating the marked occurrence of multilayer adsorption here.

It is interesting to compare the density profiles obtained in states III and IV at 50 K. Thus, at this temperature, some multilayer adsorption is already evidenced in state III (as the peak of all molecules is noticeably broader than that of the first layer ones).

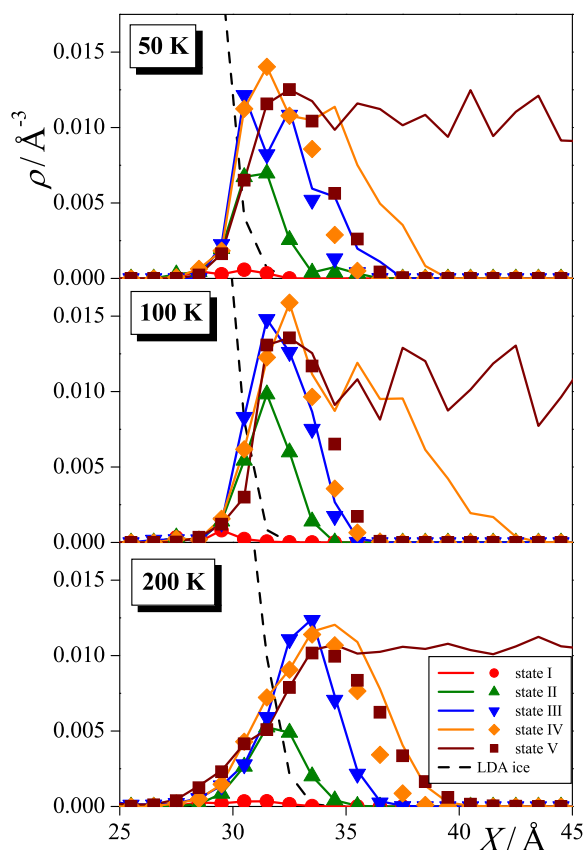


FIG. 5. Number density profile of the adsorbed acetamide molecules (lines) and of those forming the first molecular layer (symbols) at the surface of LDA ice, as obtained from the simulations of systems I (red lines, circles), II (green lines, up triangles), III (blue lines, down triangles), IV (orange lines, diamonds), and V (brown lines, squares) at 50 K (top panel), 100 K (middle panel), and 200 K (bottom panel). The surface part of the water number density profile, obtained in state I at each temperature, is also shown for reference (black dashed lines).

However, the density peak of the first layer molecules is noticeably lower here than in state IV, indicating that the first layer is not yet saturated in state III. These findings clearly reveal that at 50 K, unlike at the two higher temperatures considered, the formation of outer molecular layers starts before the first layer gets saturated. This finding can explain the observed disappearance of the plateau corresponding to the saturated monolayer at 50 K (see Fig. 2) and suggests that, with respect to water–acetamide interaction, acetamide–acetamide interaction becomes progressively stronger with the decreasing temperature. The physical reason behind this behavior might well be, at least partly, that acetamide–acetamide H-bonds are of higher entropy cost than the water–acetamide ones, as acetamide is a larger molecule, which also bears an apolar CH_3 group, and hence, the H-bonding of an acetamide molecule to another acetamide implies a stronger steric restriction and, thus, higher ordering than that of a water molecule.

It is also seen that the density peak of the first layer molecules shifts progressively farther from the LDA phase with the increasing surface coverage from state I to III at every temperature, indicating a change of the preferred orientation of the adsorbed molecules upon saturation of the first layer. This point is further addressed in Subsection IV B.

An interesting feature of the obtained acetamide density profiles is the oscillation in state V (i.e., in condensed phase acetamide), which is apparent at the two lower temperatures considered, while it is not seen at 200 K. At first sight, this finding can suggest that an ordering transition occurs in condensed phase acetamide between 100 and 200 K. However, such an ordering transition would be incompatible with the above discussed, temperature independent molar entropy of the condensed phase acetamide. To elucidate this point, we have also calculated the intrinsic density profile of the acetamide molecules in state V with respect to the (intrinsic) surface of the LDA phase. Apart from the increasing statistical noise with the decreasing temperature, these intrinsic profiles (not shown here) are, indeed, rather similar to each other, and in particular, the low temperature ones do not show the oscillatory behavior seen from the non-intrinsic ones. This finding indicates that the ordering transition occurs in the LDA phase, and the oscillations shown by the acetamide profiles simply reflect this change, as they disappear when the effect of the capillary waves of the LDA surface is removed from the acetamide profiles.

Finally, the surface concentration of the saturated monolayer can be well estimated by integrating the density peak of the first layer molecules in the presence of condensed phase acetamide (i.e., state V). This value is resulted in 8.6, 8.5, and 10.2 $\mu\text{mol}/\text{m}^2$ at 50, 100, and 200 K, respectively. Thus, the surface concentration of the saturated monolayer of acetamide at the surface of LDA ice is estimated here to be $9.1 \pm 0.8 \mu\text{mol}/\text{m}^2$.

B. Orientation of the first layer acetamide molecules

To unambiguously describe the orientation of a rigid molecule relative to an external plane or direction, two independent orientational variables are required. Therefore, the full description of the orientational statistics of the first layer acetamide molecules relative to the LDA surface can be given by the bivariate joint distribution of two such variables, such as the polar angles, θ and ϕ , of the surface normal vector in a local Cartesian frame fixed to the individual

acetamide molecules.^{67,68} Here, we consider the surface normal vector, X , pointing away from the LDA phase and define this local Cartesian frame in the following way. Its origin coincides with the N atom of the acetamide molecule, axis x points along the N–C bond from the N to C atom, and axis z is the molecular normal, directed in such a way that $\vartheta \leq 90^\circ$, and hence, $\cos \vartheta \geq 0$, while axis y is perpendicular to the above two axes, and it is oriented such that the y coordinate of the O atom is positive. The definition of this frame and that of the polar angles ϑ and ϕ are illustrated in Fig. 6. It should be emphasized that while angle ϑ is formed by two general spatial vectors, ϕ is formed by two vectors that are restricted, by definition, to lay in a given plane (i.e., the xy plane of the local frame). Therefore, uncorrelated orientation of the molecules with the LDA surface corresponds to a uniform bivariate distribution only if $\cos \vartheta$ and ϕ are chosen to be its two variables.

The $P(\cos \vartheta, \phi)$ orientational maps of the surface layer acetamide molecules are shown in Fig. 7 as obtained in states I–V at the three temperatures considered. In state I, the preferred orientation occurs at $\cos \vartheta = 1$, indicating that in this state, the adsorbed acetamide molecules prefer to lay parallel to the LDA surface. This preferred orientation is denoted here by A. [It should be noted that in the case of $\cos \vartheta = 1$, the surface normal vector, X , coincides with axis z of the local frame, and hence, angle ϕ loses its meaning; see Fig. 6. As a consequence, all points of the $P(\cos \vartheta, \phi)$ orientational map laying along the $\cos \vartheta = 1$ line correspond to the same orientation, i.e., parallel alignment with the ice surface.] With the increasing surface coverage, a new orientational preference, corresponding to the $\{\cos \vartheta = 0, \phi = 300^\circ\}$ point of the orientational map, emerges, as evidenced by the gradual shift of the peak of the $P(\cos \vartheta, \phi)$ distribution along the $\phi = 300^\circ$ line. In this preferred orientation, marked

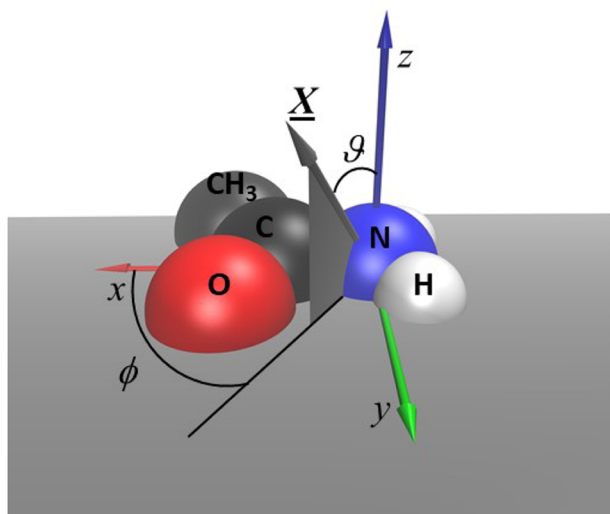


FIG. 6. Definition of the local Cartesian frame fixed to the individual acetamide molecules in the analysis of their orientational preferences and that of the polar angles ϑ and ϕ describing the orientation of the surface normal axis, X (pointing, by our definition, away from the LDA phase) in this frame. The C atom and CH_3 group, N atom, O atom, and H atoms of the reference acetamide molecule are shown by black, blue, red, and white balls, respectively.

here as **B**, the acetamide molecule stays perpendicular to the LDA surface in such a way that the C=O bond and one of the two N–H bonds are still laying more or less parallel to the surface, while the CH_3 group points away from the ice phase. The preferred alignments **A** and **B** are illustrated at the bottom of Fig. 7.

The gradual change of the orientational preference from alignment **A** to **B** occurs with the saturation of the first molecular layer, i.e., between states I and III, at each temperature. On the other hand, the building up of the outer molecular layers and, eventually, the condensation of acetamide, occurring between states III and V, are only accompanied by the gradual weakening of the preference for alignment **B** rather than by the occurrence of any marked new orientational preference of the surface molecules. These findings are in a clear accordance with the shift of the acetamide density peak farther from the LDA phase upon going from state I to III (see Fig. 5), as discussed in Subsection IV A.

The observed orientational preferences and their changes with the increasing surface coverage can be explained in the following way. At low enough surface concentrations, when the adsorbed acetamide molecules are typically isolated from each other, they try to maximize their H-bonding with the surface water molecules. In alignment **A**, all the four possible H-bonding directions of the adsorbed acetamide molecule also lay parallel to the macroscopic plane of the LDA surface, and hence, H-bonds can easily be formed with the neighboring water molecules in all of these directions. Thus, in state I, surface acetamide molecules are expected to form at least three, but, in some cases, even four H-bonds with their water neighbors. With the increasing saturation of the LDA surface, the adsorbed molecules are increasingly competing for the H-bonds with the surface waters. This increasing competition gives rise to the gradual emergence of the preference for alignment **B**, in which the adsorbed molecules occupy considerably smaller surface area (and hence higher surface concentration can be reached) than in alignment **A**. On the other hand, an acetamide molecule of orientation **B** can hardly form more than two H-bonds with the surface waters (as now one of the lone pair directions of the O atom points away from the LDA phase, and due to steric hindrances, the O atom and the N–H group being in the *cis*-position relative to it cannot participate in H-bonds at the same time). On the other hand, two neighboring acetamide molecules of alignment **B** can easily form a H-bond with each other, presumably between the O atom of one, and the N–H group being in the *trans*-position relative to the C=O bond of the other molecule. Thus, the dominance of alignment **B** in the surface layer (as seen in state III) implies that adsorbed acetamide molecules form up to two H-bonds with the surface waters and 1 or, in the case of chain formation, even two H-bonds with their acetamide neighbors.

Finally, the building up of the outer molecular layers offers the first layer acetamide molecules the possibility of H-bond formation with the outer layer ones. Since outer layer acetamide molecules are not expected to exhibit any particular orientational preference relative to the LDA surface, the increasing formation of inter-layer acetamide–acetamide H-bonds naturally leads to the observed gradual weakening of the orientational preferences within the surface layer. This change is also expected to be accompanied by the increase of the number of acetamide–acetamide H-bonds, while surface acetamide molecules might still form one or two H-bonds with the surface waters. This point is further addressed in Subsection IV C.

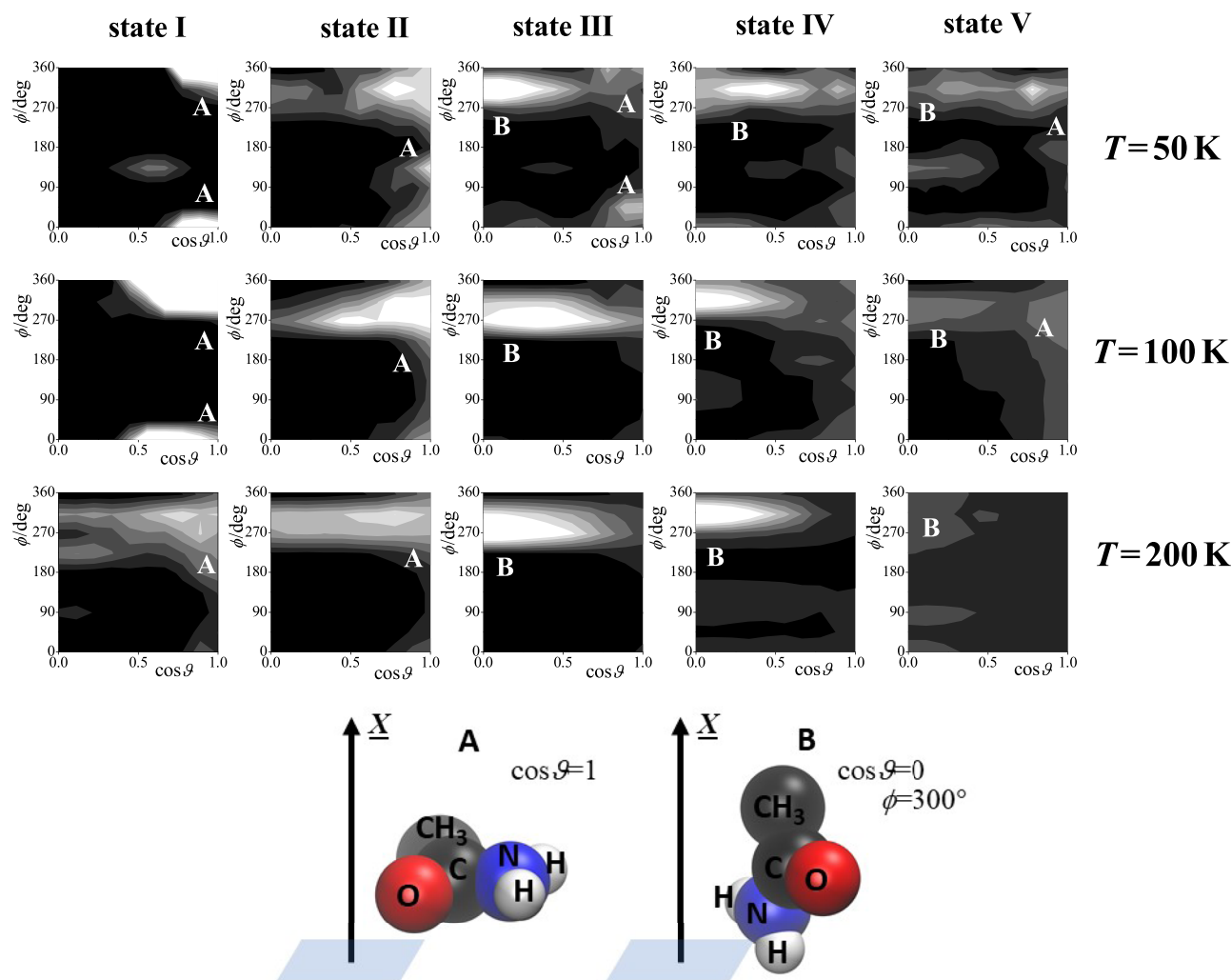


FIG. 7. Orientational maps of the first layer acetamide molecules, as obtained in states I (first column), II (second column), III (third column), IV (fourth column), and V (fifth column) from the simulations performed at 50 K (top row), 100 K (middle row), and 200 K (bottom row). Lighter shades of gray correspond to higher probabilities. Preferred orientations **A** and **B** are illustrated at the bottom; $\underline{X}$ is the surface normal axis pointing away from the LDA phase; the color coding of the atoms is the same as in Fig. 6.

Typical H-bonding patterns of the surface acetamide molecules with their water and acetamide neighbors are illustrated in Fig. 8, showing a H-bonded cluster of surface water and first layer acetamide molecules, as taken out from a simulation performed at 100 K.

C. Energetic background of the adsorption

To also investigate the energetic background of the adsorption, we have calculated the distribution of the binding energy, U_b , of the first layer acetamide molecules. The binding energy is the energy required to bring a given molecule to infinite distance; in other words, it is the interaction energy of this molecule with the rest of the system. Besides the distribution of the binding energy itself, we have also calculated those of the binding energy contributions coming from the interaction with the ice phase and with

the other adsorbed acetamide molecules, U_b^{ice} and U_b^{lat} , respectively. The $P(U_b)$, $P(U_b^{\text{ice}})$, and $P(U_b^{\text{lat}})$ distributions are shown in panels (a)–(c) of Fig. 9 as obtained in systems I–V at 50, 100, and 200 K, respectively.

The obtained distributions show the same general features at each temperature, with the obvious exception that the distributions become progressively noisier at lower temperatures. In state I, the $P(U_b^{\text{ice}})$ distribution exhibits a broad peak around -64 kJ/mol at 200 K and a similar but narrower peak at 50 K. (The split of this peak in the latter case is likely the consequence of statistical noise.) Considering that the energy of a H-bond is about -20 to -25 kJ/mol and that water–acetamide H-bonds are rather weak,⁵⁷ the position of this peak indicates that isolated acetamide molecules, indeed, typically form three H-bonds with the surface waters, and the difference of the

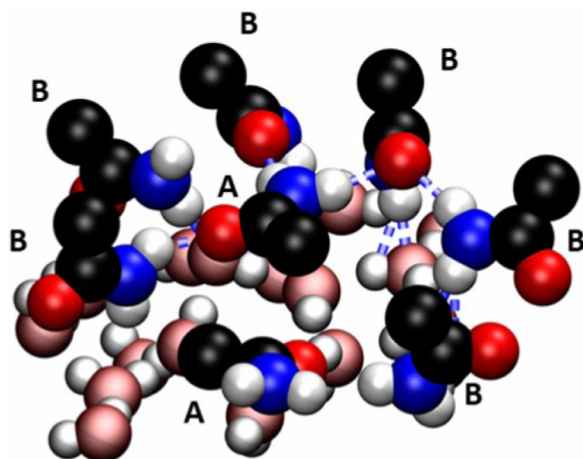


FIG. 8. H-bonded cluster of surface water and first layer acetamide molecules, as taken out from a simulation performed at 100 K, illustrating the typical H-bonding patterns of the surface acetamide molecules, aligned in one of their preferred orientations, with their water and acetamide neighbors.

peak widths at 200 and 50 K suggests that deviations from this three H-bonded pattern occur more frequently at higher temperatures. The distribution obtained at 100 K is also consistent with this picture; however, now, it exhibits three distinct peaks, occurring around -92 , -67 , and -45 kJ/mol. This split, unlike that seen at 50 K, does

have a real physical reason: the three peaks correspond to acetamide molecules, forming four, three, and two H-bonds, respectively, with the surface water molecules. The entire distribution extends from about -100 to -30 kJ/mol, similarly to what is seen at 200 K (but in a clear contrast with that at 50 K, which drops practically to zero below about -80 kJ/mol and above -50 kJ/mol). This finding suggests that two, three, and four H-bonded acetamide molecules also occur at 200 K, but these states are much less separated here than at 100 K, while at 50 K, the vast majority of the adsorbed molecules have three H-bonded water neighbors.

The mean value of this distribution can serve as a good estimate of the heat of adsorption at infinitely low surface coverage, a quantity that is relatively easily accessible by experimental methods. This value has turned out to be -67.2 , -71.7 , and -64.5 kJ/mol at 50, 100, and 200 K, respectively. Assuming that this value does not depend on the temperature, it is, thus, estimated to be -67.8 ± 3.0 kJ/mol. Unfortunately, we are not aware of any experimental study accessing this quantity; however, its measurement in the future could provide an important test of the validity of the present results.

The $P(U_b^{\text{lat}})$ distribution exhibits a very high and narrow peak in state I at zero energy; evidencing that here the vast majority of the adsorbed acetamide molecules are, indeed, isolated from each other. At 100 K, this distribution exhibits another peak around -22 kJ/mol, indicating the occurrence of H-bonded acetamide pairs even at this low surface coverage. Furthermore, due to the negligible lateral contribution to the binding energy, the $P(U_b)$ distribution is always very similar to $P(U_b^{\text{ice}})$ in state I.

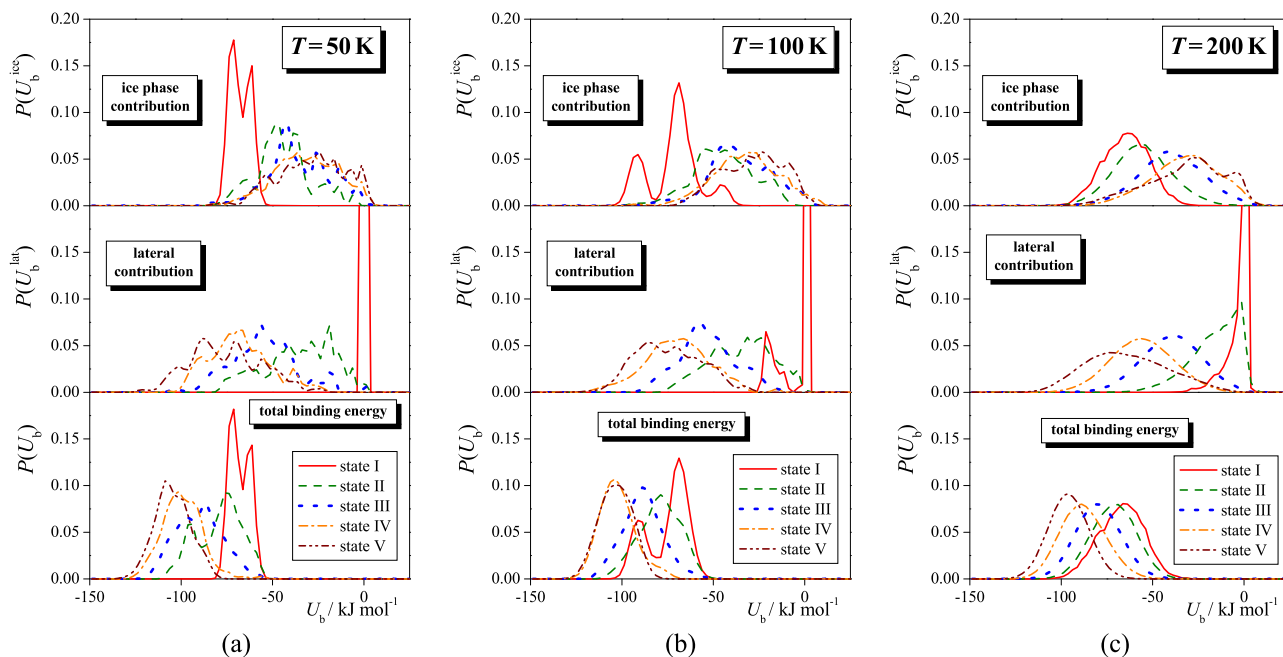


FIG. 9. Distribution of the total binding energy of the first layer acetamide molecules (bottom panels) and that of its contributions coming from the other acetamide molecules (middle panels) and from the LDA phase (top panels), as obtained at (a) 50 K, (b) 100 K, and (c) 200 K in states I (red solid lines), II (green dashed lines), III (blue dotted lines), IV (orange dashed-dotted lines), and V (brown dashed-dotted-dotted lines).

When the first molecular layer gets progressively more saturated, i.e., upon going from state I to III, the $P(U_b^{\text{ice}})$ and $P(U_b^{\text{lat}})$ distributions gradually shift to higher and lower energies, respectively, evidencing the increasing competition of the adsorbed molecules for surface positions and their increasing interaction (i.e., H-bonding) with each other. These shifts are accompanied by the gradual change of the preferred orientation from parallel to perpendicular alignment with respect to the LDA surface, seen from the shift of the peak of both the density profiles (Fig. 5) and the orientational maps (Fig. 7). Once the surface molecular layer becomes more or less saturated (i.e., in state III), the $P(U_b^{\text{ice}})$ and $P(U_b^{\text{lat}})$ distributions cover the energy ranges of about -70 to 0 and -90 to -20 kJ/mol, respectively, indicating that in this state, the adsorbed molecules can form 0–3 H-bonds with the surface water molecules and 1–4 H-bonds with each other. The mean values of these distributions, being about -30 to -40 kJ/mol for $P(U_b^{\text{ice}})$ and -40 to -55 kJ/mol for $P(U_b^{\text{lat}})$, suggest that the typical pattern here is the formation of 1–2 H-bonds with the water and the 2–3 ones with the acetamide neighbors.

It is interesting to see how the mean value of these distributions and, in particular, their difference change with the temperature. Thus, at 200 K, the mean value of both $P(U_b^{\text{ice}})$ and $P(U_b^{\text{lat}})$ is -40.0 kJ/mol. With the decreasing temperature, $P(U_b^{\text{ice}})$ shifts to higher, while $P(U_b^{\text{lat}})$ shifts to lower energies in state III; thus, at 50 K, their mean values are already -35.2 and -54.7 kJ/mol, respectively. This finding is in a clear accordance with our earlier claim that, with the decreasing temperature, the interaction between acetamide molecules becomes more important than that between water and acetamide molecules, leading to the occurrence of outer molecular layers before the first one gets saturated at 50 K. The observed shift of the $P(U_b^{\text{ice}})$ and $P(U_b^{\text{lat}})$ distributions with the decreasing temperature clearly confirms this assumption. Furthermore, this finding can also explain the observed shrinking and eventual disappearance of the saturated monolayer plateau of the adsorption isotherm with the decreasing temperature (see Fig. 2). Thus, at 200 K, the remarkable stability of the adsorption monolayer is resulted from the fact that adsorbate-ice and lateral interactions are of the same strengths, and hence, water-acetamide and acetamide-acetamide H-bonds are exchangeable with each other for practically no energy cost. However, with the decreasing temperature, the importance of the lateral interaction increases with respect to the water-acetamide one. As a consequence, acetamide molecules start occupying positions in the outer molecular layers, while positions in the first layer are still available, resulting in the disappearance of the monolayer plateau of the adsorption isotherm.

Finally, the building up of the outer molecular layers and condensation of acetamide (i.e., the move from system III to V) is not accompanied by marked changes of the $P(U_b^{\text{ice}})$ distribution (as this change does not imply a further strong increase of the competition for the positions at the already saturated LDA surface), while the $P(U_b^{\text{lat}})$ distribution further shifts to lower energies (as new H-bonds can be formed with the increasing number of second layer acetamide neighbors). Interestingly, such a shift still occurs between states IV and V. Thus, the mean value of $P(U_b^{\text{lat}})$ is about 6 – 8 kJ/mol lower in state V than in state IV at every temperature considered. This finding suggests that the second molecular layer of the adsorbed acetamide molecules is still not fully built up even right below the point of

condensation (i.e., in state IV). In state V, the mean values of the $P(U_b^{\text{ice}})$, $P(U_b^{\text{lat}})$, and $P(U_b)$ distributions are about -30 , -70 , and -100 kJ/mol, respectively, at all the three temperatures considered, indicating that in the presence of condensed phase acetamide, the first layer acetamide molecules form all the four of their possible H-bonds, among which typically one involves a water, while the other three involve acetamide neighbors.

V. SUMMARY AND CONCLUSIONS

In this paper, the adsorption of acetamide at the surface and its dissolution in the bulk phase of LDA ice have been investigated by GCMC computer simulations in the temperature range of 50 – 200 K, characteristic of the interstellar medium. We have estimated the surface concentration of the saturated monolayer and the heat of adsorption at infinitely low surface concentration to be $9.1 \pm 0.8 \mu\text{mol/m}^2$ and -67.8 ± 3.0 kJ/mol, respectively. We have also found that the chemical potential value corresponding to the point of condensation decreases linearly with increasing temperature. Based on thermodynamic considerations, we have provided an explanation of this behavior in analogy with the Clausius–Clapeyron equation and estimated the molar entropy of the condensed phase of acetamide to be 34.0 J/mol K. Since all these above quantities are experimentally relatively easily accessible, their future measurements could provide an additional important test of validity of the present results.

We have found that the dissolution of acetamide, in clear contrast with its adsorption, is an endothermic process due to the relative weakness of the acetamide–water hydrogen bonds,⁵⁷ which have to replace stronger water–water H-bonds upon dissolution. Thus, contrary to that at 200 K,⁵³ no considerable dissolution of acetamide has been observed at lower temperatures.

The adsorption isotherm has been found to exhibit a rather interesting evolution with the temperature. Thus, at 200 K, the saturated monolayer is stable in a rather broad range of chemical potentials, while only traces of multilayer adsorption occur below the point of condensation. With decreasing temperature, the plateau of the adsorption monolayer shrinks and, eventually, vanishes at 50 K, while multilayer adsorption becomes more and more pronounced. At 50 K, outer layers even start to be populated before the saturation of the first layer. Correspondingly, the number of acetamide–acetamide H-bonds increases, while that of the acetamide–water H bonds decreases in the saturated monolayer with decreasing temperature, leading to a continuous shift of the distribution of the interaction energy of the adsorbed acetamide molecules with other acetamides, $P(U_b^{\text{lat}})$, to lower, while that with the ice phase, $P(U_b^{\text{ice}})$, to higher energies. Thus, while the mean values of the two distributions are equal to each other at 200 K, that of the former is about 1.5 times larger in magnitude than that of the latter at 50 K. These findings are explained by the higher entropy cost of the acetamide–acetamide than acetamide–water H-bonds, resulting in increasing dominance of the former one with decreasing temperature.

We have found that at low enough chemical potential values, when the adsorbed molecules are isolated from each other, they prefer to lay parallel to the ice surface in order to maximize their H-bonding with the surface water molecules. Such acetamides have,

indeed, been found to form three and, in some cases, even four acetamide–water H-bonds. Upon saturation of the first layer, the increasing competition of the adsorbed molecules for H-bonds with the surface water molecules and the possibility of their H-bond formation with each other trigger a marked change in their orientational preference. Thus, in the case of the saturated monolayer and in the presence of outer layers, acetamide molecules prefer to stay perpendicular to the surface, pointing by the CH₃ group away from the LDA phase. Correspondingly, acetamide molecules in the saturated monolayer typically form 1–2 H bonds with the surface waters and 2–3 H-bonds with each other. Furthermore, in the presence of condensed phase acetamide, H-bonds can also be formed with outer layer acetamides; thus, in these systems, the first layer acetamide molecules typically form one H-bond with their water and three with their acetamide neighbors.

Finally, concerning the question whether this adsorption is strong enough to enable the interstellar formation of peptide chains involving acetamide molecules in the reaction path, our results suggest that this might well be a plausible scenario in the low temperature (i.e., below 50 K) domains of the ISM, while this is rather unlikely in its higher temperature (i.e., 100–200 K) domains.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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