

Computer Simulation Investigation of the Adsorption of Cyanamide on Amorphous Ice at Low Temperatures

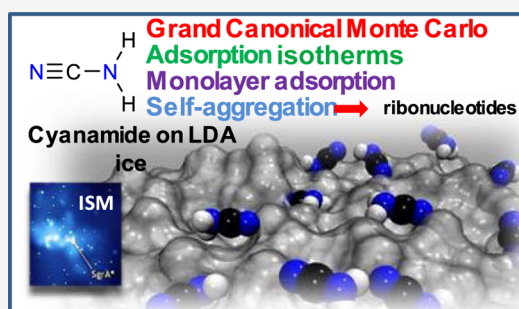
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ABSTRACT: The adsorption of cyanamide at the surface of low density amorphous (LDA) ice is studied by grand canonical Monte Carlo simulations in the temperature range of 50–200 K, under conditions characteristic of the interstellar medium and prebiotic Earth. The obtained results show that the adsorption is strictly monomolecular; moreover, condensation of cyanamide even precedes the saturation of the adsorption monolayer in the entire temperature range studied. Adsorbed cyanamide molecules are found to form altogether 3–4 hydrogen bonds with each other and with the surface water molecules at every surface concentration. As a consequence, their adsorption is strongly an exothermic process and hence becomes progressively more pronounced with decreasing temperature. Lateral H-bonding between the adsorbed cyanamide molecules leads to their noticeable clustering, evidenced also by the non-Langmuir character of the adsorption isotherm, becoming more pronounced at lower temperatures. Besides adsorption, cyanamide molecules are also found to be able to dissolve in the bulk LDA phase in a noticeable extent. However, contrary to the surface adsorption, dissolution turns out to be an entropy-driven, endothermic process and hence becomes more pronounced at higher rather than at lower temperatures.



1. INTRODUCTION

Cyanamide (aminomethanenitrile, $\text{NH}_2\text{--C}\equiv\text{N}$) is the simplest molecule that consists of both a cyano and an amino group, which enables this molecule to act both as a donor and an acceptor partner in intermolecular H-bonds with large interaction energy.¹ Cyanamide was hypothesized to be present on the primitive Earth, where its production was enabled either by electron irradiation of a mixture of methane, ammonia, and water or by the ultraviolet irradiation of aqueous NH_4CN solution.² Furthermore, the plausible formation of cyanamide and its prebiotically relevant derivatives from aqueous HCN solution was also demonstrated using advanced ab initio nanoreactor simulations.³ In the presence of liquid water, both isomerization and hydrolysis of cyanamide can be significant.⁴ Wollin and Ryan showed that an aqueous mixture of KNO_3 and NH_2CN , treated by UV radiation and electrical discharges in the presence of oxygen, resulted in the formation of nucleosides, nucleic acid bases, hydrocarbons, and organic esters after two months, while proteins were detected in the sample after 13 months.⁵ Sutherland and co-workers as well as Bracher also reported prebiotically feasible conditions that enabled the synthesis of activated pyrimidine ribonucleotides from feedstocks of simple precursors, such as glycolaldehyde, cyanamide, and phosphate.^{6,7} Further, it has been shown that precursors of ribonucleotides, amino acids, and lipids can all be derived by the reductive homologation of hydrogen cyanide and some of its derivatives, including cyanamide, and hence all

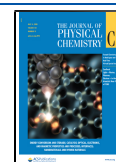
the cellular subsystems could have arisen simultaneously through common chemistry.⁸ Such reactions can, however, only occur if the reactants are available in a sufficiently high (local) concentration.

Because of its high permanent dipole moment (i.e., 4.32 ± 0.08 D),⁹ cyanamide was detected by spectral emissions coming from the Sgr B2 molecular cloud ($T < 100$ K) through its microwave transitions as the first known interstellar molecule containing the NCN frame.¹⁰ Further, cyanamide is considered to be a potential prebiotic intermediate, although its gas phase reaction can be extremely difficult due to the low temperature and concentration in the gas phase of Sgr B2 molecular cloud. Besides gas phase reactions, the chemistry of interstellar clouds can take place either at the surface or in the bulk of dust grains, where enrichment of the reactive species can occur.¹¹ The surface of the cold dust grains (10–100 K) is mainly composed of low density amorphous (water) ice (LDA).¹² Inside the molecular clouds, UV radiation can induce chemical evolution of the grain surface, leading to the

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formation of new species.¹³ Laboratory experiments showed that at low temperatures (50–140 K), cyanamide either condenses at the surface of amorphous ice or it is trapped in the bulk ice phase. After the adsorption of cyanamide, ice water was found to catalyze the isomerization of cyanamide to carbodiimide,¹⁴ while the hydrolysis of either cyanamide or carbodiimide, leading to the formation of urea or isourea, was not observed under the same experimental conditions.¹⁵ It is worthy to mention that this isomerization cannot occur in the gas phase under the thermodynamic conditions of the interstellar clouds.¹⁶ Cyanamide also readily dimerizes and trimerizes to dicyandiamide (NH₂)₂CNCN¹⁷ and melamine,¹⁸ respectively. Melamine, a possible component of proto-RNA,¹⁹ has also been reported to be identified in the Orgueil meteorite.²⁰ Based on these findings, it can be hypothesized that these essential biological building blocks can be delivered to Earth from the interstellar medium (ISM).

To understand the cyanamide chemistry in the ISM, a detailed characterization of its adsorption at the surface of LDA ice is therefore of key importance. Further, possible enrichment of cyanamide in an aqueous environment can be critical toward cyanamide oligomerization, which may be a key for the early stage of chemical evolution. As in the case of HCN, where evidences for the synthesis of nitrogen-containing species of potential prebiotic interest is favored in the ice matrix following a freezing concentration model,²¹ icy surfaces might also act as cyanamide concentrators. However, the extreme conditions of the ISM make the experimental investigation of this adsorption rather complicated. On the other hand, experimental investigations can be conveniently complemented by studies employing computer simulation methods,²² in which a suitably chosen model of the system of interest is seen at atomistic resolution, and extreme conditions can relatively easily be accessed. In studying adsorption, the grand canonical Monte Carlo (GCMC) method^{22,23} is particularly suitable because in a GCMC simulation, the chemical potential rather than the number of the adsorbate molecules is fixed. Thus, performing a set of GCMC simulations in which the adsorbate chemical potential is systematically varied and, as its function, the number of adsorbed molecules is determined, the adsorption isotherm can readily be calculated. Indeed, the GCMC method was successfully applied to investigate the adsorption of a number of small adsorbate molecules on various adsorbents, such as self-assembled monolayers,^{24,25} carbonaceous materials,^{26–28} metal oxides,^{29–31} clay minerals,^{32,33} zeolites,^{34,35} covalent organic frameworks,^{36,37} protein crystals,³⁸ clathrate hydrates,^{39–43} and crystalline^{44–52} and amorphous ice.^{52,53}

In this paper, we investigate in detail the adsorption of cyanamide at the surface of LDA ice under interstellar conditions (i.e., in the temperature range of 50–200 K) by GCMC computer simulations. Besides determining the adsorption isotherm at three temperatures, i.e., at 50, 100, and 200 K, the properties of the adsorption layer, the preferred surface orientations of the adsorbed molecules, and the energetic background of the adsorption are analyzed in detail. The relation of the lateral interaction of the adsorbed molecules as well as of the adsorbate–adsorbent interaction with the properties of the isotherm, the possible dissolution of the cyanamide molecules to the bulk LDA phase, and the possible relevance of these processes under conditions characteristic to the ISM and to the prebiotic Earth are discussed in detail. The paper is organized as follows. In

Section 2, details of the calculations performed are given. The obtained results are presented and discussed in Section 3. Finally, in Section 4, the main conclusions of this study are summarized.

2. COMPUTATIONAL DETAILS

The adsorption of cyanamide on LDA ice has been investigated by performing three sets of Monte Carlo simulations on the grand canonical (μ, V, T) ensemble at the temperatures of 50, 100, and 200 K, respectively. The LDA phase consisted of 2880 water molecules. In these sets of simulations, the chemical potential of cyanamide has been systematically varied from values corresponding to practically no adsorbed molecules to the bulk condensed phase of cyanamide. The chemical potential values considered in the simulations, together with the average number of cyanamide molecules found in the basic box are summarized in Tables 1–3. The X, Y, and Z edges of the rectangular basic simulation box have been 100, 35.926, and 38.891 Å long, respectively, with X being the macroscopic surface normal axis.

Table 1. Adsorption Isotherm of Cyanamide on LDA Ice at 50 K, As Obtained from the Simulations

$\mu/\text{kJ mol}^{-1}$	$\langle N \rangle$	p/p_0	$\Gamma/\mu\text{mol m}^{-2}$
−66.40	1.013	2.72×10^{-19}	6.02×10^{-2}
−64.32 ^a	2.966	4.03×10^{-17}	0.176
−62.25	7.642	5.98×10^{-15}	0.454
−60.17	8.009	8.88×10^{-13}	0.476
−58.09	12.40	1.32×10^{-10}	0.737
−56.01	19.30	1.96×10^{-8}	1.15
−53.93	24.48	2.90×10^{-6}	1.45
−51.85	33.90	4.31×10^{-4}	2.01
−49.78 ^b	74.18	6.39×10^{-2}	4.41
−48.74 ^c	93.29	0.779	5.54
−48.53	850.1		
−46.87	852.7		
−45.20	847.2		
−43.54 ^d	853.3		

^aState I. ^bState II. ^cState III. ^dState IV.

Cyanamide molecules have been described by the OPLS-AA force field^{54,55} augmented with the OPLS-AA compatible

Table 2. Adsorption Isotherm of Cyanamide on LDA Ice at 100 K, As Obtained from the Simulations

$\mu/\text{kJ mol}^{-1}$	$\langle N \rangle$	p/p_0	$\Gamma/\mu\text{mol m}^{-2}$
−65.09 ^a	3.915	1.96×10^{-8}	0.233
−63.01	6.312	2.38×10^{-7}	0.375
−60.93	9.501	2.90×10^{-6}	0.565
−58.85	14.25	3.54×10^{-5}	0.847
−56.77	22.04	4.31×10^{-4}	1.31
−54.69	34.75	5.25×10^{-3}	2.06
−53.03 ^b	49.95	3.88×10^{-2}	2.97
−52.20	71.52	0.105	4.25
−50.54 ^c	117.1	0.779	6.95
−50.12	848.2		
−49.29	840.1		
−48.04 ^d	858.2		
−46.79	860.8		

^aState I. ^bState II. ^cState III. ^dState IV.

Table 3. Adsorption Isotherm of Cyanamide on LDA Ice at 200 K, As Obtained from the Simulations

$\mu/\text{kJ mol}^{-1}$	$\langle N \rangle$	p/p_0	$\Gamma/\mu\text{mol m}^{-2}$
−64.56	0.6512	7.85×10^{-4}	3.87×10^{-2}
−62.89	1.674	2.13×10^{-3}	9.95×10^{-2}
−61.23 ^a	2.976	5.80×10^{-3}	0.177
−59.57	8.647	1.58×10^{-2}	0.514
−57.90	11.91	4.29×10^{-2}	0.708
−56.24	31.52	0.116	1.87
−54.58 ^b	55.24	0.317	3.28
−53.75	72.37	0.522	4.30
−52.92	100.9	0.861	5.99
−52.75 ^c	107.4	0.951	6.38
−52.58 ^d	820.1		
−52.08	840.6		
−51.25	847.3		
−49.59	861.6		

^aState I. ^bState II. ^cState III. ^dState IV.

1.14*CM1A-LBCC charge model for the Coulomb interaction, where the point charges have been generated by LigParGen.⁵⁶ Recently, the performance of the 1.14*CM1A-LBCC charge model with the OPLS-AA force field for a data set of 426 free energies of hydration was thoroughly examined by Dodda et al.⁵⁷ The mean absolute deviation of the free energies of hydration was found to be only 0.61 kcal/mol, while the average errors of the computed heats of vaporization and densities of pure organic liquids were also found to be rather small (i.e., 1.40 kcal/mol and 0.024 g/cm³, respectively).⁵⁷ Water molecules have been modeled by the four-site TIP4P/Ice potential,⁵⁸ which gives an excellent description of the properties of the solid phases of water. According to these potential models, the total energy of the system has been assumed to be the sum of the interaction energies of all molecular pairs, while the interaction energy of a molecular pair has been calculated as the sum of the Lennard-Jones and Coulomb contributions of all pairs of their interaction sites. The interaction parameters (i.e., Lennard-Jones distance and energy parameters, σ and ϵ , respectively, and fractional charges, q) are summarized in Table 4. The Lennard-Jones parameters

Table 4. Interaction Parameters of the Molecular Models Used

molecule	site	$\sigma/\text{\AA}$	$\epsilon/\text{kJ mol}^{-1}$	q/e
cyanamide	H			0.3922
	N(H)	3.30	0.711	−0.7507
	C	3.65	0.628	0.3368
	N	3.20	0.711	−0.3705
water	O	3.1668	0.8821	
	H			0.5897
	M ^a			−1.1794

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

of unlike atom pairs have been determined using the Lorentz–Berthelot combination rules²² (i.e., arithmetic mean for σ and geometric mean for ϵ). According to the original parametrization of the OPLS-AA force field,^{54,55} all interactions have been truncated to zero beyond the center–center cut-off distance of 12.5 Å. It should also be emphasized that because we are interested here in single molecule (rather than

collective) properties of cyanamide, the results are not supposed to be sensitive to the long-range correction employed, as it was earlier demonstrated on the example of the adsorption of acetone on ice.⁴⁶ The geometry of the molecules has been kept unchanged in the simulations; the bond lengths and bond angles of the models used are collected in Table 5.

Table 5. Geometry Parameters of the Molecular Models Used

molecule	bond	bond length (Å)	angle	bond angle (deg)
cyanamide	N≡C	1.17		
	C–N	1.34		
	N–H	1.01		
			N≡C–N	177.44
water			C–N–H	114.82
			H–N–H	112.53
	O–H	0.9572		
	O–M	0.1577		
			H–O–H	104.52

The simulations have been performed using the code MMC.⁵⁹ In a Monte Carlo step, either a randomly chosen molecule (either a water or a cyanamide) has been 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°, or the number of the cyanamide molecules in the basic box has been attempted to be changed by 1 by either inserting or deleting a molecule. Particle displacement and insertion/deletion attempts have been performed in an alternating order; in the latter case, particle insertions and deletions have been attempted with equal probabilities. Insertion/deletion steps have been done using the cavity biased scheme of Mezei,^{60,61} i.e., cyanamide molecules have only been attempted to be inserted into pre-existing spherical cavities with a minimum radius of 2.5 Å. Suitable cavities have been searched for along a 100 × 100 × 100 grid in the basic box, which has been regenerated after every 10⁶ Monte Carlo steps. Particle displacement and insertion/deletion attempts have been accepted or rejected according to the standard Metropolis criterion^{22,62} and to the acceptance rules of the cavity biased method,^{60,61} respectively. The probability of finding a suitable cavity for insertion, P_{cav} , a parameter included in the acceptance rule of the cavity biased insertions and deletions, has simply been estimated as the ratio of the cavities found, and grid points checked.

The LDA–vapor interface has been created in the following way. First, the required number of 2880 water molecules has randomly been placed in a rectangular basic box; the Y and Z axes of which have already been set to their final values, while the length of the X axis has been chosen in such a way that the density of the system has corresponded to the experimental density of bulk liquid water. The system has then been equilibrated by performing 3 × 10⁸ Monte Carlo steps at 300 K, followed by another 10⁸ steps at 200 K. Then, the LDA–vapor interface has been created by enlarging the X edge of the basic box to its final value of 100 Å. The interfacial system has further been equilibrated in a 10⁷ steps long trajectory at 300 K, followed by another 10⁷ steps long trajectory at 250 K, and a 3 × 10⁷ steps long trajectory at 200 K. At the beginning of each simulation, 2 cyanamide molecules have randomly been placed to the vapor phase of

the system. Then, in the GCMC runs, the systems have been equilibrated by performing 5×10^9 to 2×10^{10} Monte Carlo steps, depending on the temperature and cyanamide chemical potential, until the number of cyanamide molecules in the basic box has been relaxed and fluctuated around its equilibrium value. The average number of cyanamide molecules in the basic box, $\langle N \rangle$, has then been averaged over 2×10^9 equilibrium configurations. It should be emphasized that because the position of the water molecules has also been changed, the structure of the LDA phase and its surface has also been properly sampled in the simulations. Finally, at selected chemical potential values (see Tables 1–3), 2500 equilibrium sample configurations, separated from each other by 10^6 Monte Carlo steps long trajectories each, have been saved from the subsequent, 2.5×10^9 Monte Carlo steps long run for the detailed analyses. Equilibrium snapshots of the system simulated, obtained at 100 K at three selected chemical potential values, are shown from top view in Figure 1a. Further, equilibrium snapshots of the systems containing condensed phase of cyanamide are shown from side view in Figure 1b, as obtained at the three temperatures considered.

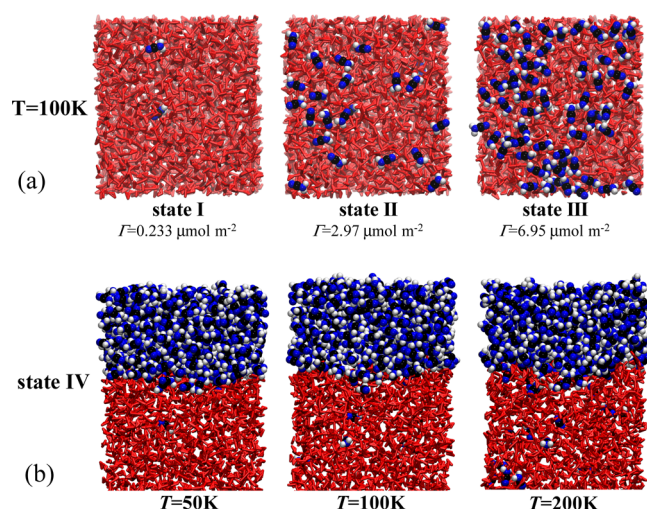


Figure 1. Equilibrium snapshots of the system simulated (a) at 100 K at three selected chemical potential values, corresponding to states I–III (see Table 2), from top view, and (b) at the three temperatures considered at chemical potential values corresponding to the condensed phase of cyanamide, from side view. Cyanamide N, C, and H atoms are represented by blue, black, and white balls, respectively, while water molecules are shown by red sticks.

3. RESULTS AND DISCUSSION

3.1. Adsorption Isotherms. The average number of cyanamide molecules found in the basic box, $\langle N \rangle$, is plotted against their chemical potential (μ) in Figure 2, as obtained from the GCMC simulations at the three temperatures considered; the corresponding values are also collected in Tables 1–3. At every temperature, $\langle N \rangle$ gradually increases with μ up to a certain chemical potential value, at which it exhibits a sudden jump and above which it remains more or less constant. This sudden jump of the $\langle N \rangle(\mu)$ curves corresponds to the condensation of cyanamide: above this μ value, the basic box is filled with cyanamide molecules. The chemical potential value corresponding to the condensation, denoted here as μ_0 , is found to be -52.666 kJ/mol at 200 K,

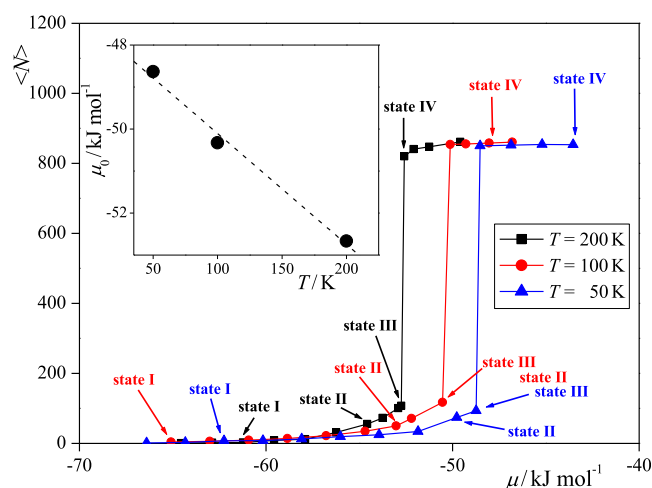


Figure 2. Number of cyanamide molecules in the basic simulation box as a function of their chemical potential, as obtained from the simulations performed at 200 K (black squares), 100 K (red circles), and 50 K (blue triangles). The lines connecting the points are just guides to the eye. The arrows indicate the states in which sample configurations have been saved for detailed analyses. The inset shows the temperature dependence of the chemical potential value corresponding to the point of condensation (filled circles) together with their linear fit (dashed line).

-50.328 kJ/mol at 100 K, and -48.632 kJ/mol at 50 K. The obtained $\mu_0(T)$ data follow a linear trend, as shown in the inset of Figure 2. It should be noted that although the value of $\langle N \rangle$ as well as the slope of the $\langle N \rangle(\mu)$ curve increases gradually with μ below the point of condensation, no drastic increase of the slope is seen at the vicinity of μ_0 , suggesting that the adsorption of cyanamide is restricted to one molecular layer. This point will be further addressed later in this paper.

To further analyze the adsorption isotherms, we have converted them to the more conventional Γ versus p_{rel} form, where Γ is the surface concentration of cyanamide, i.e.,

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

(where the factor of 2 in the denominator accounts for the two LDA surfaces in the basic box) and $p_{\text{rel}} = p/p_0$ is the relative pressure, i.e., the pressure of the system, p , normalized by that of the saturated vapor of cyanamide at the temperature considered, p_0 . The value of p_{rel} can be calculated through μ_0 as³⁰

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

where k_B is the Boltzmann constant. It should be emphasized that because p_0 is the vapor pressure of cyanamide corresponding to the point of condensation, p_{rel} becomes meaningless above this point, and thus, the $\langle N \rangle(\mu)$ data can only be converted to $\Gamma(p_{\text{rel}})$ in the μ range below the point of condensation. The Γ and p_{rel} values of the systems simulated are indicated in Tables 1–3, and the $\Gamma(p_{\text{rel}})$ data are also shown in Figure 3, as obtained at the three temperatures considered. Clearly, the slope of these isotherms at low pressures increases strongly with decreasing temperature. We have fitted the obtained $\Gamma(p_{\text{rel}})$ data by the Langmuir isotherm,^{63,64} i.e.,

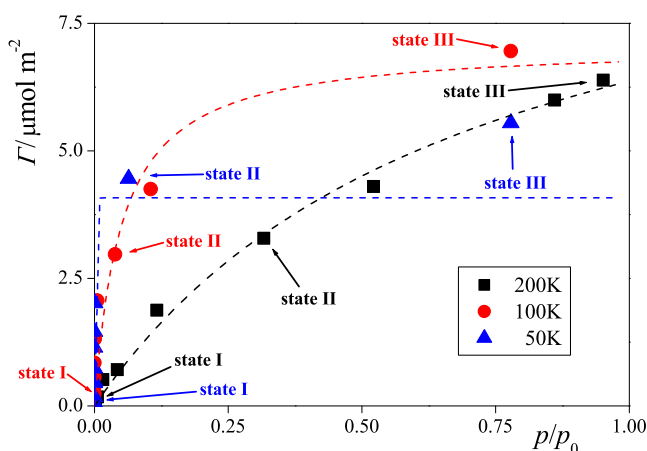


Figure 3. Adsorption isotherms of cyanamide on LDA ice in the Γ vs p_{rel} form, as obtained from the simulations performed at 200 K (black squares), 100 K (red circles), and 50 K (blue triangles). The Langmuir isotherms (see eq 3) best fitting the simulation data are shown by dashed lines. The arrows indicate the states in which sample configurations have been saved for detailed analyses.

$$\Gamma = \Gamma_{\text{max}} \frac{p_{\text{rel}} K}{1 + p_{\text{rel}} K} \quad (3)$$

where Γ_{max} and K are the surface concentration of the saturated monolayer and the Langmuir partition coefficient between the adsorption layer and the vapor phase, respectively. However, although the $\Gamma(p_{\text{rel}})$ data do not exhibit any sign of multilayer adsorption, the obtained data could not be well fitted by the Langmuir isotherm at any temperature, and the deviation of the fitted function from the simulated data becomes larger at lower temperatures, as seen from Figure 3. Considering also that the functional form of the Langmuir isotherm is based on the assumptions that (i) the adsorption is strictly restricted to one molecular layer and (ii) lateral interactions between the adsorbed molecules are negligible, the failure of the Langmuir fit of the simulated $\Gamma(p_{\text{rel}})$ data suggests that there are probably rather strong lateral interactions between the cyanamide molecules, leading to their self-association within the adsorption layer. This assumption seems to be reasonable considering also that cyanamide molecules can act both as H-donor and H-acceptor partners in hydrogen bonds, and hence they can easily form H-bonds with each other. This point is further investigated in a subsequent sub-section of this paper.

To address the question whether the obtained isotherms indicate the possible formation of a cyanamide adsorption layer of non-negligible surface concentration at LDA surfaces under interstellar conditions, the p_{rel} values corresponding to the simulations have to be converted to pressure (or gas phase concentration), which requires to know the saturated vapor pressure, p_0 . The temperature dependence of p_0 is described by the Antoine equation⁶⁵

$$\log_{10} p_0 = A - \frac{B}{T + C} \quad (4)$$

where the values of the Antoine parameters for cyanamide are $A = 10.14855$, $B = 3905.528$ K, and $C = 1.212$ K, and the value of p_0 is in kPa units.⁶⁶ Unfortunately, the range of validity of these parameters is only between 273 and 298 K,⁶⁶ well above the temperature range considered in the present study. Thus,

here we use a very crude upper estimate of p_0 , i.e., its value corresponding to 273 K (i.e., the lower boundary of this range of validity) of 0.06 Pa. This way, the gas phase concentrations of cyanamide required to the surface concentrations of 0.5, 1, and 2 $\mu\text{mol}/\text{m}^2$ can be estimated as 0.02, 20, and 7×10^6 molecules/ dm^3 , respectively, at 50 K, and 5×10^4 , 2×10^6 , and 10^7 molecules/ dm^3 , respectively, at 100 K. It should be stressed that these values are very crude upper estimates of the real concentrations, which might well be several orders of magnitude smaller. To get an estimate of the typical concentration of cyanamide in the ISM, we consider that Hüttemeister reported the column and volume densities of H_2 toward the low density envelope of the Sgr B2 cloud of about 10^{23} and 10^3 molecules/ cm^3 , respectively,⁶⁷ while the column density of cyanamide was found to be in the range between 2×10^{13} and 6×10^{14} molecules/ cm^2 .¹⁰ Assuming proportionality between the column and volume densities, the volume density (i.e., concentration) of cyanamide can be estimated to be in the order of 10^{-3} molecules/ dm^3 . This value is rather close to our very crude upper estimate of 0.02 molecules/ dm^3 , needed to reach a surface concentration of 0.5 $\mu\text{mol}/\text{m}^2$ at 50 K, but gets progressively farther from it with increasing surface concentration and temperature. However, considering also that our above estimates of the gas phase concentration corresponding to certain surface concentrations overestimate the real value by several orders of magnitude, and this overestimation becomes more serious at lower temperatures, our results suggest that the formation of a reasonably dense adsorption layer of cyanamide at the surface of LDA ice is a thermodynamically favored process at least in some, typically low temperature parts of the ISM.

3.2. Properties of the Adsorption Layer. To analyze the structural and energetic properties of the adsorption layer in detail, we have saved 2500 sample configurations of the system simulated at selected chemical potential values at each temperature considered. The μ values chosen for the detailed analyses correspond to (i) adsorption layers in which the cyanamide molecules are isolated from each other (referred to here at each temperature as state I), (ii) unsaturated adsorption layers, corresponding to the surface concentration value roughly half of that right below the point of condensation (referred to here as state II), and (iii) as much saturated adsorption monolayer as possible (i.e., just before the point of condensation, referred to as state III). For reference, such sampling has also been performed at a μ value corresponding to the condensed phase of cyanamide (state IV). The μ values corresponding to states I–IV at each temperature are indicated in Tables 1–3 as well as in Figures 2 and 3.

To analyze the arrangement of the cyanamide molecules along the macroscopic surface normal axis, X , we have calculated their number density profile along this axis in states I–III and, for reference, also in state IV at each temperature considered. (In these calculations, the position of a cyanamide molecule has been represented by that of its C atom.) The obtained density profiles are shown in Figure 4. For reference, the interfacial portion of the density profile of the water molecules forming the LDA phase is also indicated (as obtained in state I at each temperature). Clearly, below the point of condensation (i.e., in states I–III), the cyanamide density profiles show one single peak in the X range where the water density drops to zero, and they become practically zero in the vapor phase. On the other hand, in certain cases, the cyanamide density does not drop to zero within the LDA

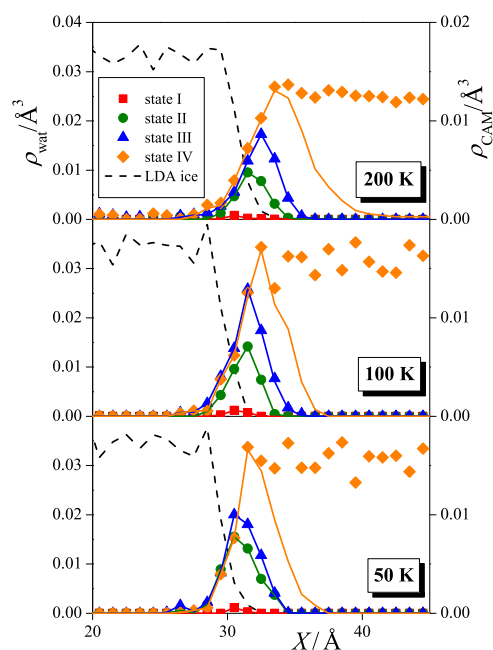


Figure 4. Number density profile of the cyanamide molecules, ρ_{CAM} , along the surface normal axis, X , as obtained from the simulations in states I (red squares), II (green circles), III (blue triangles), and IV (orange diamonds) at 200 K (top panel), 100 K (middle panel), and 50 K (bottom panel). Solid lines show the density profiles of the first molecular layer of cyanamide at the LDA surface, as obtained from the ITIM analysis. The interfacial portion of the number density profile of the water molecules forming the LDA phase, ρ_{wat} , is also shown for reference, as obtained in state I at each temperature (black dashed lines). All profiles shown are symmetrized over the two LDA surfaces present in the basic box. Scales on the left and right refer to the densities of water and cyanamide, respectively.

phase, indicating that cyanamide molecules can also be dissolved in the LDA phase, in a clear accordance with experimental observations.¹⁴ This dissolution is found not to be very strong; it is usually limited to 1–3 cyanamide molecules in the entire basic box. Nevertheless, it is clear that this dissolution becomes more pronounced with increasing temperature, suggesting that it is an endothermic, entropy-driven process. This finding can be understood considering that cyanamide molecules that are dissolved in the LDA phase probably cannot replace waters in the tetrahedral H-bonding network of LDA, and hence, unlike the water molecules themselves, they cannot form 4 H-bonds in the bulk LDA phase with the surrounding waters. Besides this energy loss, however, the dissolution of cyanamide is accompanied by the obvious entropy gain coming from the mixing of the two types of molecules and by the entropy gain associated with the destruction of the rather ordered, tetrahedrally coordinated local structure of LDA ice. Because the obtained number of the cyanamide molecules dissolved in the LDA phase is subject of rather large statistical noise, here we limit ourselves only to estimate the solubility of cyanamide in LDA ice at the three temperatures considered through the number of dissolved molecules in state IV, i.e., in the presence of condensed phase cyanamide. Integration of the cyanamide density profiles up to the point where the main density peak vanishes, i.e., 27.5 Å, results in the average number of dissolved cyanamide molecules of 1, 5, and 25 in the basic box at 50, 100, and

200 K, respectively. Estimating the boundary of the LDA phase by the X value of 30 Å, at which the water density drops to half of its bulk LDA phase value, the above values correspond to the LDA phase cyanamide concentrations of 0.02, 0.10, and 0.5 M, respectively. It should be noted that even in the case of largest dissolution observed, i.e., in state IV at 200 K, the LDA phase consists of only 1 mol % cyanamide. In order to exclude dissolved cyanamide molecules when analyzing the properties of the adsorption layer, the cyanamide molecules located in the range of $X < 25$ Å have been excluded from the subsequent analyses. Because of the small amount of the dissolved cyanamide molecules, the use of such a simple cut-off has been sufficient to distinguish between the adsorbed and the dissolved molecules.

To demonstrate that the adsorption layer is indeed restricted to one single molecular layer, we have performed ITIM analysis⁶⁸ of the sample configurations (i.e., determined the list of the cyanamide molecules that are located at the real, capillary wave corrugated surface of the LDA phase). In these analyses, a probe sphere of the radius of 2 Å and a grid line spacing of 0.5 Å have been used, and the analyses have been performed by the freely available⁶⁹ PYTIM program package.⁷⁰ The density profiles of these truly interfacial cyanamide molecules (solid lines in Figure 4) have turned out to be practically identical with those of all cyanamide molecules in states I–III in every case, confirming that in these systems all (non-dissolved) cyanamide molecules are indeed located at the boundary of the vapor and LDA phases, and hence the adsorption layer is indeed monomolecular. It is also seen that, interestingly, the average position of the adsorbed cyanamide molecules along the macroscopic surface normal axis, X , gets gradually farther from the bulk LDA phase with increasing surface coverage. This finding reveals that, at low surface coverages, adsorbed molecules prefer to stay in the troughs (i.e., surface portions of negative local curvature), where they can be well surrounded by neighboring water molecules. With increasing surface coverages, these positions gradually become occupied, and the adsorbed molecules can only find positions that are farther from the bulk LDA phase along the macroscopic surface normal axis.

We have also performed ITIM analysis in state IV at each temperature to determine the molecules forming the surface layer of the condensed phase of cyanamide. The density profiles of this surface layer, also shown in Figure 4, always go at higher densities than those of states I–III. This finding reveals that the adsorption layer of cyanamide is not just strictly monomolecular, but it is far from being saturated even in state III, i.e., right before the point of condensation at every temperature considered here. It should finally be noted that although the surface concentration of the saturated monolayer cannot be derived from the Langmuir fit of the $\Gamma(p_{\text{rel}})$ data due to the poor quality of the fit, in particular, at large p_{rel} values (see Figure 3), it can be rather accurately estimated from the surface concentration of the first molecular layer in state IV (i.e., condensed cyanamide), determined from the ITIM analysis. Assuming that the concentration of the saturated monolayer is temperature independent, the value of Γ_{max} is estimated to be $11.0 \pm 0.8 \mu\text{mol}/\text{m}^2$ this way.

3.3. Surface Orientation of the Adsorbed Molecules.

Because the orientation of a rigid particle relative to an external direction (e.g., the surface normal axis) can fully be described by two independent orientational variables, the full description of the orientational statistics of such particles relative to a

(planar) external surface requires the calculation of the joint bivariate distribution of these variables.^{71,72} Clearly, the angular polar coordinates, ϑ and ϕ , of the surface normal vector in a local Cartesian frame fixed to the individual molecules is a sufficient choice for such an independent orientational variable pair.^{71,72} In describing the surface orientation of the adsorbed cyanamide molecules, we have defined this local Cartesian frame in the following way. The origin of this frame is fixed to the N atom of the NH_2 group of the cyanamide molecule, axis z points along the $\text{N}-\text{C}\equiv\text{N}$ axis of the molecule from the NH_2 to the $\text{C}\equiv\text{N}$ nitrogen atom, axis y is parallel with the line joining the two H atoms, while axis x is perpendicular to these two axes, and it is oriented in such a way that the x coordinates of the two H atoms are positive. The definition of this local frame as well as of the polar angles, ϑ and ϕ , of the macroscopic surface normal vector, pointing, by our convention, from the LDA to the vapor phase, $\underline{X}$, is illustrated in Figure 5. It should be noted that, because of the

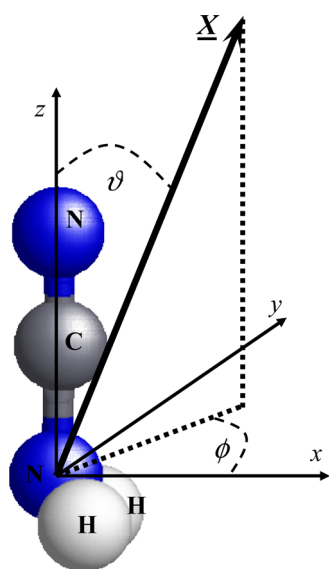


Figure 5. Definition of the local Cartesian frame fixed to the individual cyanamide molecules and of the polar angles ϑ and ϕ , describing the orientation of the molecule relative to the surface normal vector, pointing from the LDA to the vapor phase, $\underline{X}$. N, C, and H atoms are shown by blue, grey, and white balls, respectively.

planar symmetry of the cyanamide molecule, this frame is always chosen in such a way that the polar angle ϕ does not exceed 180° . Further, because ϑ is the angle between two general spatial vectors, but 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), uncorrelated orientation of the adsorbed molecules with the surface results in uniform distribution only if $\cos \vartheta$ and ϕ are chosen to be the orientational variables.^{71,72}

The $P(\cos \vartheta, \phi)$ orientational maps of the cyanamide molecules adsorbed at the LDA surface are shown in Figure 6, as obtained in states I–III at the three temperatures considered. As is expected, the bivariate distribution becomes less smooth with decreasing temperature and surface concentration, reflecting the less effective sampling in such states. Nevertheless, the orientational maps exhibit, in general, two characteristic peaks. The first of these peaks, occurring around the $\{\cos \vartheta = 0, \phi = 0^\circ\}$ point of the maps, corresponds

to the orientation in which the $\text{N}-\text{C}\equiv\text{N}$ axis of the cyanamide molecule lays parallel with the macroscopic plane of the LDA surface, and the two H atoms point toward the LDA phase. This preferred alignment of the adsorbed cyanamide molecules is referred to here as orientation A. The other preferred orientation, denoted here by B, corresponds to the $\{\cos \vartheta = 0, \phi = 180^\circ\}$ point of the maps. In this alignment, the $\text{N}-\text{C}\equiv\text{N}$ axis is again parallel with the macroscopic plane of the LDA surface; however, now the two H atoms point away from the LDA phase. The peaks corresponding to alignments A and B are indicated on the orientational maps, and these preferred alignments of the cyanamide molecules are also illustrated in Figure 6.

It should be noted that an adsorbed cyanamide molecule can form up to 4 hydrogen bonds with its neighbors, as both of its N atoms can accept one H-bond, and both of its H atoms can be donated in a H-bond. To address the possible H-bonding between the adsorbed cyanamide and surface water molecules, we have calculated the radial distribution functions (rdfs) between the water O atoms (denoted here as O_w) and the amine and cyano N atoms of cyanamide (denoted here as N_a and N_c , respectively), as well as between the potential bonding H atoms of the water molecules (H_w) and cyanamide amine groups (H_a) and their potential acceptor atoms, i.e., N_a and N_c for H_w and O_w for H_a . The rdfs obtained at 100 K in state III are shown in Figure 7 (similar curves have been obtained at other temperatures and surface coverages). As is seen, all rdfs that involve a H atom exhibit a peak around $1.95 \text{ \AA}$, while the two O–N rdfs have a peak around $2.9 \text{ \AA}$, indicating that all possible H-bonds between the adsorbed cyanamide and surface water molecules indeed occur with certain probabilities. Further, among these possible water–cyanamide H-bonds the highest populated one involves the acceptance of an amine H atom of cyanamide by a water O atom. It should also be recalled that the water molecules staying at the surface of LDA ice do not exhibit marked orientational preferences (see Figure 7 of ref 53) and also that the surface of the LDA phase is corrugated, on the molecular length scale, by capillary waves, and hence it consists of troughs and crests of molecular size. Considering these suggests that both of the preferred orientations of the cyanamide molecules might well correspond to the formation of 2–3 hydrogen bonds between the adsorbed molecules and the LDA surface, and even the formation of 4 H-bonds between a cyanamide molecule and the surrounding waters cannot be excluded in cases of lucky local arrangements of the surface water molecules around the cyanamide molecule. Further, in their preferred orientations, two neighboring adsorbed cyanamide molecules can also easily form a H-bond with each other, and hence, in the case of high surface concentrations, a cyanamide molecule can easily be involved in lateral H-bonding both with its NH_2 and $\text{C}\equiv\text{N}$ groups. This point is further addressed in the following subsection. Some snapshots showing typical H-bonding arrangements of adsorbed cyanamide molecules and their neighbors are shown in Figure 8, as taken out from the simulation performed in state I at 200 K.

3.4. Energetics of the Adsorption. To investigate the energetic background of the adsorption, we have calculated the total binding energy of the adsorbed cyanamide molecules, U_b , i.e., the energy of their interaction with the rest of the system. Further, the contributions of U_b coming from the interactions of the adsorbed molecule solely with the LDA phase and solely with the other cyanamide molecules, U_b^{ice} and U_b^{lat} , respectively,

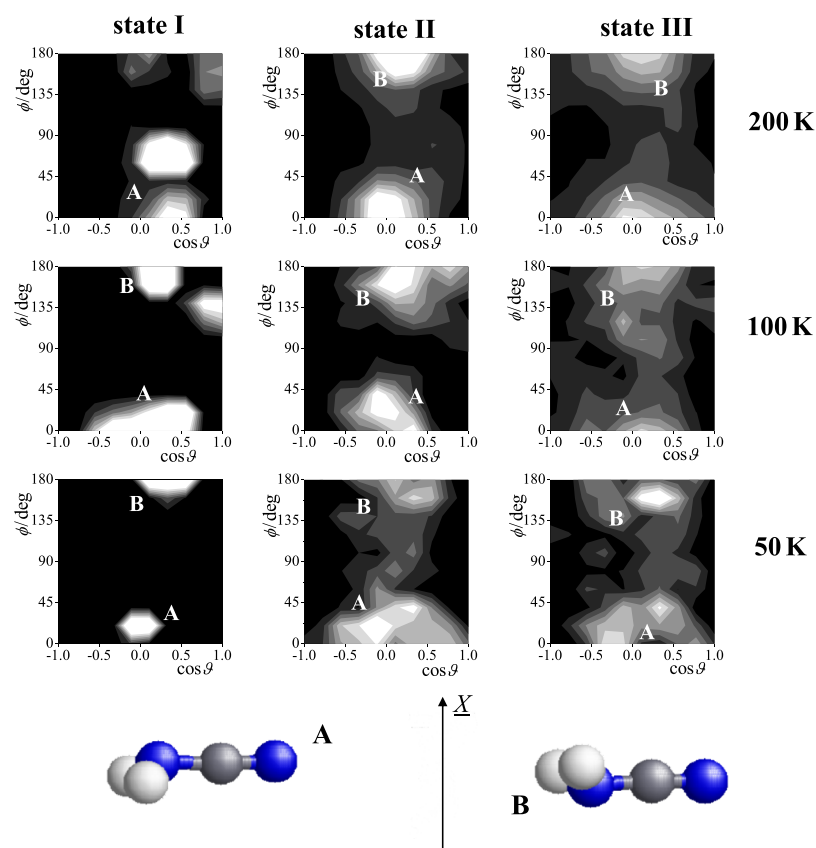


Figure 6. Orientational maps of the cyanamide molecules adsorbed at the LDA surface, as obtained at 200 K (top row), 100 K (middle row), and 50 K (bottom row) in states I (left column), II (middle column), and III (right column). Lighter shades of grey correspond to higher probabilities. Preferred orientations A and B are indicated on the maps and are also illustrated below the maps. Color coding of the atoms is the same as in Figure 5; $\hat{X}$ is the surface normal axis pointing from the LDA to the vapor phase.

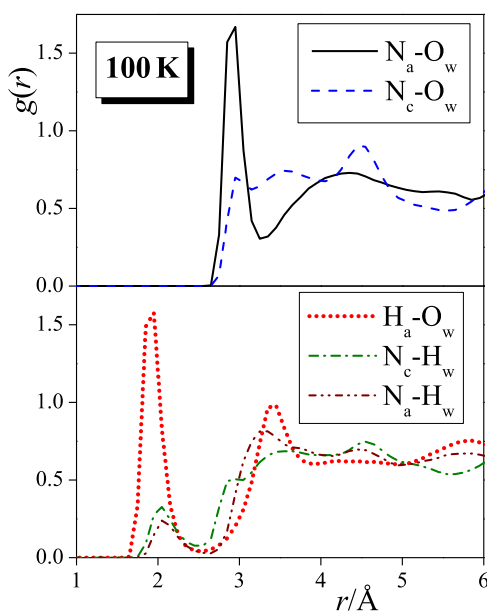


Figure 7. Radial distribution function of the water O—cyanamide amine N (black solid line) and water O—cyanamide cyano N (blue dashed line) atoms (top panel), as well as of the water O—cyanamide H (red dotted line), water H—cyanamide cyano N (green dash-dotted lines), and water H—cyanamide amine N (brown dash-dot-dotted lines) atoms, as obtained from the simulation at 100 K in state III.

have also been calculated. The distributions of U_b and of its LDA and lateral contributions, U_b^{ice} and U_b^{lat} , respectively, are shown in Figure 9a–c, as obtained at 200, 100, and 50 K, respectively, in states I–III.

As is seen, the $P(U_b^{\text{ice}})$ distribution, obtained at 200 K in state I (Figure 9a), exhibits its main peak around -100 kJ/mol, which is followed by a marked shoulder around -75 kJ/mol. In state II, this shoulder becomes the main peak of the distribution, while any trace of a peak around -100 kJ/mol is already disappeared. Finally, in state III, the peak of the $P(U_b^{\text{ice}})$ distribution occurs around -55 kJ/mol. Considering that the interaction energy of a H-bonded molecule pair is around -25 kJ/mol, these findings indicate that (i) at low enough surface concentrations, the adsorbed cyanamide molecules can indeed find local arrangements of the surface water molecules where they can form up to 4 cyanamide–water H-bonds, (ii) with increasing surface concentration, the number of H-bonds an adsorbed cyanamide molecule forms with the surrounding waters gradually decreases to 3 and then to 2, and (iii) even in the case of the most saturated adsorption monolayer that can be reached before condensation of cyanamide occurs, the adsorbed cyanamide molecules are still anchored to the LDA surface by at least two hydrogen bonds.

In state I, the distribution of the lateral contribution to the total binding energy, $P(U_b^{\text{lat}})$, at 200 K exhibits a sharp peak around zero energy and also a small peak around -25 kJ/mol. While the former of these peaks corresponds to the cyanamide molecules that are isolated from each other, the latter one

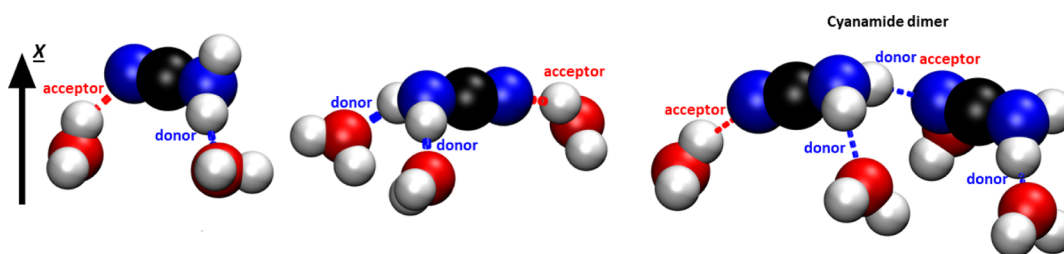


Figure 8. Snapshots showing typical arrangements of the adsorbed cyanamide molecules, together with their H-bonded neighbors, as taken out from the simulation of state I at 200 K. Left: a cyanamide molecule forming two H-bonds with surface waters; middle: a cyanamide molecule forming three H-bonds with surface waters; right: two cyanamide molecules forming a H-bond with each other and also two H-bonds each with surface waters. O, N, C, and H atoms are shown by red, blue, grey, and white balls, respectively. $\underline{X}$ is the surface normal axis pointing from the LDA to the vapor phase.

evidences the occurrence of H-bonded cyanamide pairs in the adsorption layer even at such a low surface concentration. With increasing surface concentration, the peak corresponding to the isolated cyanamide molecules decreases, and it completely disappears in state III, while the peak around -25 kJ/mol gradually increases and broadens toward lower energy values, extending beyond -50 kJ/mol already in state II. These findings suggest that cyanamide molecules exhibit a tendency for lateral self-association. Neighboring cyanamide molecules form H-bonds with each other, and although the main preference of these molecules is to have only one H-bonded cyanamide neighbor, a non-negligible fraction of them has two, indicating that, besides dimers, even H-bonded cyanamide trimers are formed at the LDA surface. These results are in line with the total binding energies obtained previously from B3LYP/aug-cc-pVDZ density functional calculations for the cyanamide dimer having two identical H-bonds and for the trimer of ladder arrangement of -41.5 and -75.7 kJ/mol, respectively.¹

The distribution of the total binding energy, $P(U_b)$, does not depend substantially on the cyanamide surface concentration, having its main peak between -75 and -100 kJ/mol (although in state I, this peak splits to a narrow peak around -100 kJ/mol and a shoulder around -75 kJ/mol), indicating that the adsorbed cyanamide molecules always form 3 or 4 H-bonds with their neighbors, and the gradual decrease of the average number of cyanamide–water H-bonds with increasing surface concentration is compensated by the increasing number of the lateral, cyanamide–cyanamide H-bonds. Similar picture is seen at lower temperatures, although the obtained distributions become increasingly noisy with decreasing temperature due to the less efficient sampling. In particular, we refrain here from interpreting the split peak of the $P(U_b^{\text{ice}})$ and $P(U_b)$ distributions in state I at 50 K, as this feature is most likely the consequence of insufficient statistics rather than the real physical behavior of the adsorbed molecules.

It should finally be noted that the mean value of U_b^{ice} in state I, i.e., when the lateral contribution to the total binding energy is negligible, can be used to estimate the heat of adsorption at infinite dilution. For this purpose, we have added the term RT (R being the gas constant) to the mean values of U_b^{ice} and obtained the values of -85.0 , -86.0 , and -89.2 kJ/mol at 50, 100, and 200 K, respectively. Assuming that this value is temperature-independent, the present simulations provide thus -86.7 ± 1.8 kJ/mol as an estimate for the heat of adsorption of cyanamide on LDA ice at infinite dilution. Unfortunately, we are not aware of any experimental data in this respect; nevertheless, experimental determination of this value in the

future in the temperature range of 50–200 K can provide a stringent test of the validity of the present results.

4. CONCLUSIONS

In this paper, the adsorption of cyanamide on LDA ice has been studied by computer simulation methods in the temperature range between 50 and 200 K, characteristic to certain parts of the ISM and of the prebiotic Earth. The obtained adsorption isotherms have revealed that this adsorption is strictly limited to a monomolecular layer, and this layer does not get fully saturated at all even at the point when condensation of cyanamide occurs. The surface concentration of the saturated monolayer has been estimated to be 11.0 ± 0.8 $\mu\text{mol}/\text{m}^2$ from the density profile of the first molecular layer in the presence of condensed cyanamide.

Although the adsorption of cyanamide is limited to one single molecular layer, the adsorption isotherms have been found to deviate considerably from the Langmuir shape, indicating that the adsorption sites are not uniformly filled; instead, the cyanamide molecules have a tendency for lateral self-association. This finding is corroborated by the results corresponding to the distributions of the binding energy of the adsorbed molecules. Thus, it has been found that pairs of adsorbed cyanamide molecules can form H-bonds with each other even at very low surface concentrations. Further, at higher surface concentrations, an adsorbed molecule has typically 1–2 H-bonded cyanamide and 2–3 H-bonded water neighbors. Thus, adsorbed cyanamide molecules have typically 3–4 H-bonded neighbors at every surface concentrations and only the ratio of the water and cyanamide molecules among these neighbors changes (i.e., decreases) with increasing surface concentration. To maximize the number of their H-bonded neighbors, adsorbed cyanamide molecules are preferentially aligned in such a way that their $\text{N}-\text{C}\equiv\text{N}$ axis lays parallel with the macroscopic plane of the LDA surface.

As a consequence of the large number of H-bonds, the cyanamide molecules form at the LDA surface, and their adsorption is accompanied by very large energy gain: the heat of adsorption at infinitely low surface concentration is estimated to be -86.7 ± 1.8 kJ/mol. Being a strongly exothermic process, the adsorbed state of cyanamide is progressively shifted to lower relative pressures with decreasing temperature. Our results indicate that the formation of the adsorption layer of non-negligible (i.e., 0.5 – 2 $\mu\text{mol}/\text{m}^2$) surface concentration, and hence, due to the strong tendency for lateral self-association, the occurrence of H-bonded cyanamide dimers and small clusters at the surface of LDA

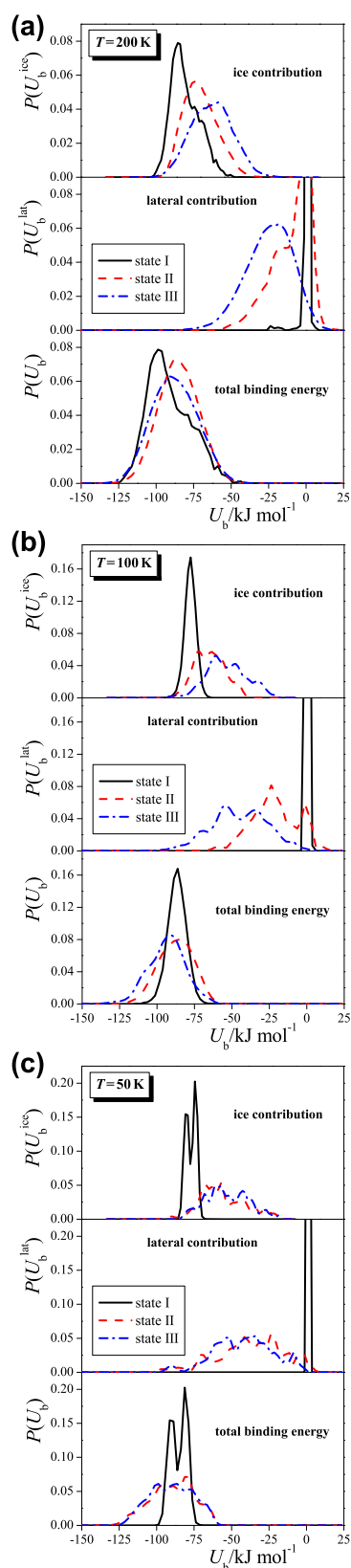


Figure 9. Distribution of the total binding energy of the adsorbed cyanamide molecules at the LDA surface (bottom panels) as well as its contributions coming from the interactions with the other adsorbed cyanamide molecules (middle panels) and with the LDA phase (top panels), as obtained from the simulations in states I (black solid lines), II (red dashed lines), and III (blue dash-dotted lines) at (a) 200, (b) 100, and (c) 50 K.

ice is thermodynamically preferred at least in some parts of the ISM.

Finally, it should be noted that, besides its strong ability for adsorption, cyanamide has also been found to be dissolved in the bulk phase of LDA ice in a non-negligible amount. However, in contrast with their surface adsorption, the dissolution of cyanamide in LDA ice has found to be an endothermic, entropy-driven process, which becomes progressively more pronounced at higher temperatures, being thus relevant under the conditions characteristic to the prebiotic Earth rather than to the ISM.

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Notes

The authors declare no competing financial interest.

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