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Calculation of the Adsorption Isotherm of Formaldehyde on Ice by Grand Canonical Monte Carlo Simulation

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The adsorption isotherm of formaldehyde at the surface of I_h ice has been calculated at 200 K by performing a set of grand canonical Monte Carlo simulations, systematically varying the chemical potential of formaldehyde. In a clear contrast to other partially oxidized small hydrocarbons (POHs), such as methanol, the obtained isotherm does not show any particular stability of the saturated adsorption monolayer of the formaldehyde molecules. Further, in contrast to that of methanol, the obtained adsorption isotherm can be well described with the functional form of the Langmuir isotherm, indicating the relative weakness of the lateral interactions between the adsorbed molecules. The obtained results show that the main thermodynamic driving force of the adsorption is the possibility of the formation of water–formaldehyde hydrogen bonds. However, an adsorbed formaldehyde molecule has never been found to form more than one hydrogen bond with the surface waters, and due to the requirement of maximizing the number of water–formaldehyde hydrogen bonds per surface unit, these hydrogen bonds are often rather distorted, hence they are relatively weak in the case of the saturated adsorption monolayer. Besides these water–formaldehyde hydrogen bonds, the adsorbed molecules are further stabilized by lateral dipole–dipole type interactions, which are, however, considerably weaker than the water–formaldehyde hydrogen bonds, and also weaker than the lateral hydrogen bonding that occurs in the adsorption layer of other POH molecules, such as methanol.

1. Introduction

Small, partially oxidized hydrocarbons (POHs) such as methanol (CH_3OH) and formaldehyde (HCHO) play important roles in the chemistry of the upper troposphere. In this cold environment their photooxidation can provide a substantial source of HO_x radicals, which drive photochemical cycles involving ozone production and loss in the atmosphere.¹ Because the upper troposphere is characterized by the presence of cirrus clouds largely made of ice particles, not only gas-phase processes are of importance, but also trace gas interactions at the surface of ice have to be taken into account to better understand the physicochemical behavior of this region of the atmosphere. Besides, the influence of gas/ice interactions on the atmospheric chemistry of POHs above snow covered surfaces has also been recently evidenced.^{2–4} Therefore, the knowledge of the exchange between the atmosphere and the underlying snowpack is of particular importance for the development of transfer functions that link concentrations in the snowpack and in the gas phase above polar regions. Among the various POH molecules, particular attention has been devoted in recent studies to formaldehyde,^{5–10} because its photolysis produces oxidizing radicals that enhance the oxidizing capacity of the atmosphere in polar regions, where other sources of these radicals are reduced.

In a more general way, understanding the possible exchange of POHs between ice (or snow) particles and the lower

atmosphere requires the knowledge of their incorporation, diffusion, and release mechanisms in ice (snow) crystals. Therefore, a growing number of experimental^{11–18} and theoretical^{19–24} studies have been recently devoted to the characterization of the interactions between POHs and ice. More specifically, Knudsen cell and coated-wall flow tube experiments have been performed to characterize the influence of various organic functional groups (e.g., $\text{C}=\text{O}$, $\text{O}-\text{H}$, $\text{C}(\text{O})\text{OH}$, $\text{C}(\text{O})\text{H}$) on the interactions between ice surfaces and different POHs, including ketones,^{13,16,17} alcohols,^{11,14} carboxylic acids,^{12,18,22} and aldehydes.^{11,14} These studies have shown that the interaction between POHs and ice is of the simplest type, i.e., reversible physisorption. The corresponding adsorption enthalpies have been measured within the range between -70 and -50 kJ/mol for all these organic molecules, with the exception of formaldehyde. Indeed, in opposition to the other POHs, the formaldehyde uptake of ice does not show any noticeable temperature dependence, at least at low enough pressures, precluding experimental determination of the adsorption energy.¹¹ Results of a recent theoretical study of ours have led to rather similar conclusions. In this study we have calculated the adsorption free energy of various small, isolated trace-gas molecules, including several POHs at the free ice/vapor surface. The resulting values have scattered between -18 and -24 kJ/mol for all the POH molecules considered, with the exception of formaldehyde, for which the adsorption free energy value of only -11.7 kJ/mol was obtained.²⁴

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Several further theoretical investigations, including ab initio calculations²⁰ as well as molecular dynamics (MD) simulations,²¹ have also been devoted to the interaction of formaldehyde and ice. In the ab initio calculations based on the periodic Hartree–Fock method, two adsorption sites on the ice surface have been considered, for a coverage corresponding to one formaldehyde molecule per unit cell of proton-ordered ice. In the first adsorption site, the equilibrium configuration corresponds to a location of the formaldehyde molecule above a dangling hydrogen, with the C=O axis oriented perpendicular to the ice surface. In this configuration, the adsorption energy ranges from -19.4 to -26.3 kJ/mol, depending on the ab initio level of the calculations. In the second adsorption site, located on top of the center of a hexagonal ring of water molecules, the formaldehyde molecule lies parallel to the ice surface at equilibrium, with an adsorption energy ranging from -22.7 to -33.7 kJ/mol.²⁰ This second configuration is similar to the one evidenced in MD simulations at finite temperature and for surface densities ranging from low coverage to the saturation coverage of one monolayer. Indeed, in the MD simulation, the formaldehyde molecules were found to be adsorbed with a nearly flat orientation on the ice surface, the CO axis of the molecule being directed toward the ice surface with a tilt angle of 10° with respect to the plane parallel of the ice surface. The adsorption energy in MD simulations is about -30.0 kJ/mol.²¹ The energies calculated from ab initio or MD approaches are considerably higher (i.e., smaller in magnitude) than the values calculated for other POHs, such as acetone^{19,20} and methanol,²¹ and can, at least partly, explain the low affinity of formaldehyde for the ice surface.

To study the adsorption phenomena by theoretical methods, the grand canonical Monte Carlo (GCMC) simulation method^{25,26} is a particularly suitable tool, because it allows a direct theoretical determination of adsorption isotherms by keeping the temperature constant and controlling the chemical potential of the adsorbed molecules. This method has been used to simulate adsorption on fixed substrates, such as carbonaceous materials^{27–32} and silica substrates.^{33,34} It has also been successfully used very recently to simulate adsorption of methanol molecules on ice at tropospheric conditions,³⁵ with the simulated isotherm showing a remarkable agreement with experimental measurements.^{11,35}

In the present paper, we present results of GCMC calculations of the adsorption isotherm of formaldehyde on ice at 200 K. This theoretical study aims at characterizing the details of formaldehyde–ice interactions, and at understanding the experimentally measured differences with other molecules of similar size, such as methanol. For this purpose, we extensively compare the presently obtained results with those obtained recently in a similar study of ours, characterizing the adsorption of methanol on ice.³⁵ The drawn conclusions are not only based on the calculation of the adsorption isotherm, but also are supported by a detailed analysis of the energy and surface orientation of the adsorbed formaldehyde molecules at various surface coverage values.

The paper is organized as follows. In section 2 details of the calculations are given. The obtained results, concerning the adsorption isotherm, the energetic background of the adsorption, and the surface orientation of the adsorbed formaldehyde molecules, are presented and discussed in section 3. Finally, in section 4 the main conclusions of this study are summarized.

2. Computer Simulations

The adsorption isotherm of formaldehyde on ice has been calculated by performing a set of Monte Carlo simulations on

TABLE 1: Data of the Adsorption Isotherm of Formaldehyde on Ice, as Obtained from Our Simulations

B	$\mu/\text{kJ mol}^{-1}$	$\langle N \rangle$	$\Gamma/\mu\text{mol m}^{-2}$	p/p_0
0.0	−27.03	869.7		
−1.0	−28.69	846.6		
−1.2	−29.02	837.7		
−1.6	−29.68	828.8		
−1.7	−29.84	228.4	13.62	0.951
−1.8	−30.01	167.5	9.99	0.861
−2.0	−30.34	154.3	9.20	0.705
−2.2	−30.67	143.6	8.57	0.577
−3.0	−32.00	95.5	5.69	0.259
−4.0	−33.65	49.3	2.94	9.53×10^{-2}
−5.0	−35.31	26.5	1.58	3.51×10^{-2}
−6.0	−36.97	13.9	0.83	1.29×10^{-2}
−7.0	−38.62	6.5	0.39	4.75×10^{-3}
−8.0	−40.28	3.1	0.19	1.75×10^{-3}
−9.0	−41.93	1.4	0.08	6.43×10^{-4}
−10.0	−43.59	0.6	0.04	2.36×10^{-4}

the grand canonical (μ, V, T) ensemble at 200 K. The X , Y , and Z edges of the rectangular basic simulation box have been set to 100.0, 35.926, and 38.891 Å, respectively. The ice phase, placed in the middle of the basic box along its edge X that is perpendicular to the ice surface, has been built up by 18 molecular layers of proton-disordered I_h ice, as described in our previous papers.^{24,35} Each layer consisted of 160 water molecules. The lengths of the Y and Z edges of the basic box have been set in accordance with the geometry of this crystal. The molecules belonging to the two innermost layers have been kept fixed in the simulations. The reason for fixing these two layers of the ice crystal is to stabilize the bulk phase of the ice crystal. However, in order to check the importance of this treatment, we have repeated the $B = -1.8$ simulation with letting also the water molecules of these two layers move. Apart from a small increase of the ice phase density, the results obtained this way do not differ noticeably from those obtained by fixing these water molecules. The chemical potential of the formaldehyde molecules has been controlled through the B parameter of Adams,²⁵ related to the chemical potential through the equation

$$\mu = k_B T \left(B + \ln \frac{\Lambda^3}{V} \right) \quad (1)$$

where T and V are the temperature and volume of the system, k_B is the Boltzmann constant, and Λ is the thermal de Broglie wavelength of formaldehyde:

$$\Lambda = \frac{h}{\sqrt{2\pi k_B T m}} \quad (2)$$

where m is the mass of a formaldehyde molecule.

Simulations have been performed with 16 different B values, corresponding to the μ range between -27.0 and -43.6 kJ/mol. The B and μ values as well as the average number of formaldehyde molecules in the basic box $\langle N \rangle$ are summarized in Table 1.

Water molecules have been described by the rigid, five-site TIP5P model,³⁶ whereas for formaldehyde a rigid potential model³⁷ belonging to the OPLS family has been used. In this water model the positively charged H atoms and the sites carrying negative fractional charges (denoted by “L”) are located at the distances of 0.9572 and 0.70 Å, respectively, from the O atom, whereas the H–O–H, L–O–L, and L–O–H angles are 104.5° , 110.7° , and 109.5° , respectively. In the planar formaldehyde model the H–C and C=O bonds are 1.101 and 1.203 Å long, respectively, and the H–C=O angle is 121.8° .

TABLE 2: Interaction Parameters of the Water and Formaldehyde Potential Models Used in the Simulations

molecule	interaction site	$\sigma/\text{\AA}$	$(\epsilon/k_B)/\text{K}$	q/e
water	O	3.120	80.6	0.000
	H	0.000	0.0	+0.241
	L	0.000	0.0	-0.241
formaldehyde	C	3.750	52.9	+0.450
	O	2.960	105.8	-0.450
	H	2.420	7.6	0.000

In this model only the C and O atoms carry fractional charges (i.e., $+0.45e$ and $-0.45e$, respectively); hence the 2.6 D dipole moment of the model points along the O=C double bond. The interaction of two molecules is calculated as the sum of the Lennard-Jones and charge-charge Coulomb interactions of all the possible pairs of their interaction sites. The fractional charges q and Lennard-Jones distance and energy parameters σ and ϵ of the different sites of these models are summarized in Table 2.

The simulations have been performed using the program MMC.³⁸ Standard periodic boundary conditions have been applied. All interactions have been truncated to zero beyond the molecule-based cutoff distance of 12.5 Å. In accordance with the original parametrization of the potential models used,^{36,37} no long-range correction has been applied for the electrostatic interactions. To check the importance of the treatment of the long-range part of the electrostatic interactions, we have repeated the $B = -1.8$ simulation using the reaction field correction method^{39,40} under conducting boundary conditions (i.e., the dielectric constant of the background continuum has been set to infinity instead of 1). No noticeable difference between the calculated properties has been observed, apart from a small, trivial shift of the binding energy distributions to lower values (due to the fact that now the electrostatic interactions of the distant pairs have also been accounted for).

In the simulations, particle displacement and insertion/deletion steps have been performed in alternating order. In a particle displacement step a randomly chosen molecule has been randomly translated by no more than 0.25 Å and randomly rotated around a randomly chosen space-fixed axis by no more than 15°. Formaldehyde and water molecules (excluding the molecules belonging to one of the two innermost layers of ice) have been selected for this move in alternating order. In a particle insertion/deletion step either a randomly chosen formaldehyde molecule has been attempted to be removed from the system, or an extra formaldehyde molecule has been tried to be inserted to the system. These two types of moves have been attempted with equal probabilities. The insertion/deletion steps have been done using the cavity biased algorithm of Mezei.^{41,42} Insertions have only been attempted into cavities of the minimum radius of 2.5 Å. Suitable cavities have been searched for along a $100 \times 100 \times 100$ grid. To remove the bias introduced into the sampling by making insertion attempts into the centers of such cavities only, the acceptance probability of the insertion and deletion moves has to be corrected by the factor of $\ln P_{\text{cav}}^N$, where P_{cav}^N is the probability of finding a suitable cavity in a configuration containing N formaldehyde molecules. The value of P_{cav}^N has simply been calculated as the ratio of the grid points that are located inside a suitable cavity and the total number of grid points checked in the configurations containing exactly N formaldehyde molecules.

The systems have been equilibrated by performing 10^8 Monte Carlo moves. Then 2×10^8 equilibrium configurations have been generated for the calculation of $\langle N \rangle$. In the case of two systems, i.e., the ones that are characterized by the chemical

potential values of $\mu = -33.65$ kJ/mol and $\mu = -30.01$ kJ/mol (corresponding to low surface coverage of ice and to the presence of a saturated monolayer of formaldehyde, respectively) 2500 sample configurations, separated by 4×10^4 Monte Carlo steps each, have been saved for further analyses. An instantaneous equilibrium snapshot of the $\mu = -30.01$ kJ/mol system is shown in Figure 1.

3. Results and Discussion

3.1. Adsorption Isotherm. The adsorption isotherm $\langle N \rangle(\mu)$ obtained from the simulations is shown in Figure 2. The obtained curve increases with increasing steepness up to the point (i.e., about $\mu = -29.75$ kJ/mol) where the condensation of formaldehyde occurs. In other words, no plateau corresponding to the existence of the saturated adsorption layer within a broad range of chemical potential values appears on the isotherm. This behavior is in clear contrast to what has recently been observed for the adsorption of methanol.³⁵ To clearly demonstrate this difference between the adsorption behaviors of methanol and formaldehyde on ice, the adsorption isotherm calculated recently for methanol is shown in the inset of Figure 2.

The lack of the plateau corresponding to the saturated monolayer of the formaldehyde molecules indicates that this saturated adsorption layer is not particularly stable. This fact might be originated either in the weakness of the interaction of the adsorbed formaldehyde molecules with the ice phase or in the lack of strong lateral interactions between the adsorbed molecules. To further investigate this problem, we have converted the obtained adsorption isotherm to the $\Gamma(p_{\text{rel}})$ form, where Γ is the surface density of the adsorbed molecules and p_{rel} is the pressure of the vapor phase p normalized by the pressure of the saturated vapor of formaldehyde p_0 . The value of p_{rel} can simply be calculated, using the relation⁴³

$$B = \ln \frac{pV}{k_B T} \quad (3)$$

as

$$p_{\text{rel}} = \frac{p}{p_0} = \frac{\exp B}{\exp B_0} \quad (4)$$

In this equation B_0 denotes the B value at which the condensation of formaldehyde occurs. This value is found to be $B_0 = -1.65$ here. The value of Γ has simply been given as

$$\Gamma = \frac{\langle N \rangle}{2YZ} \quad (5)$$

assuming that all the formaldehyde molecules that are in the system are adsorbed at the ice surface, and taking into account the fact that, due to the periodicity of the system, the ice phase has two surfaces in the basic box. The above assumption has been found to be correct up to the point where the condensation of formaldehyde occurs. However, since eq 3 holds only in the vapor phase, the $\Gamma(p_{\text{rel}})$ isotherm can only be calculated up to the point of condensation. The calculated isotherm is shown in Figure 3 in the $\Gamma(p_{\text{rel}})$ form, whereas the p_{rel} and Γ values corresponding to the simulations performed are included in Table 1.

The obtained $\Gamma(p_{\text{rel}})$ data can be described in terms of the Langmuir isotherm, i.e., by the function

$$\Gamma = \Gamma_{\text{max}} \frac{p_{\text{rel}} K}{p_{\text{rel}} K + 1} \quad (6)$$

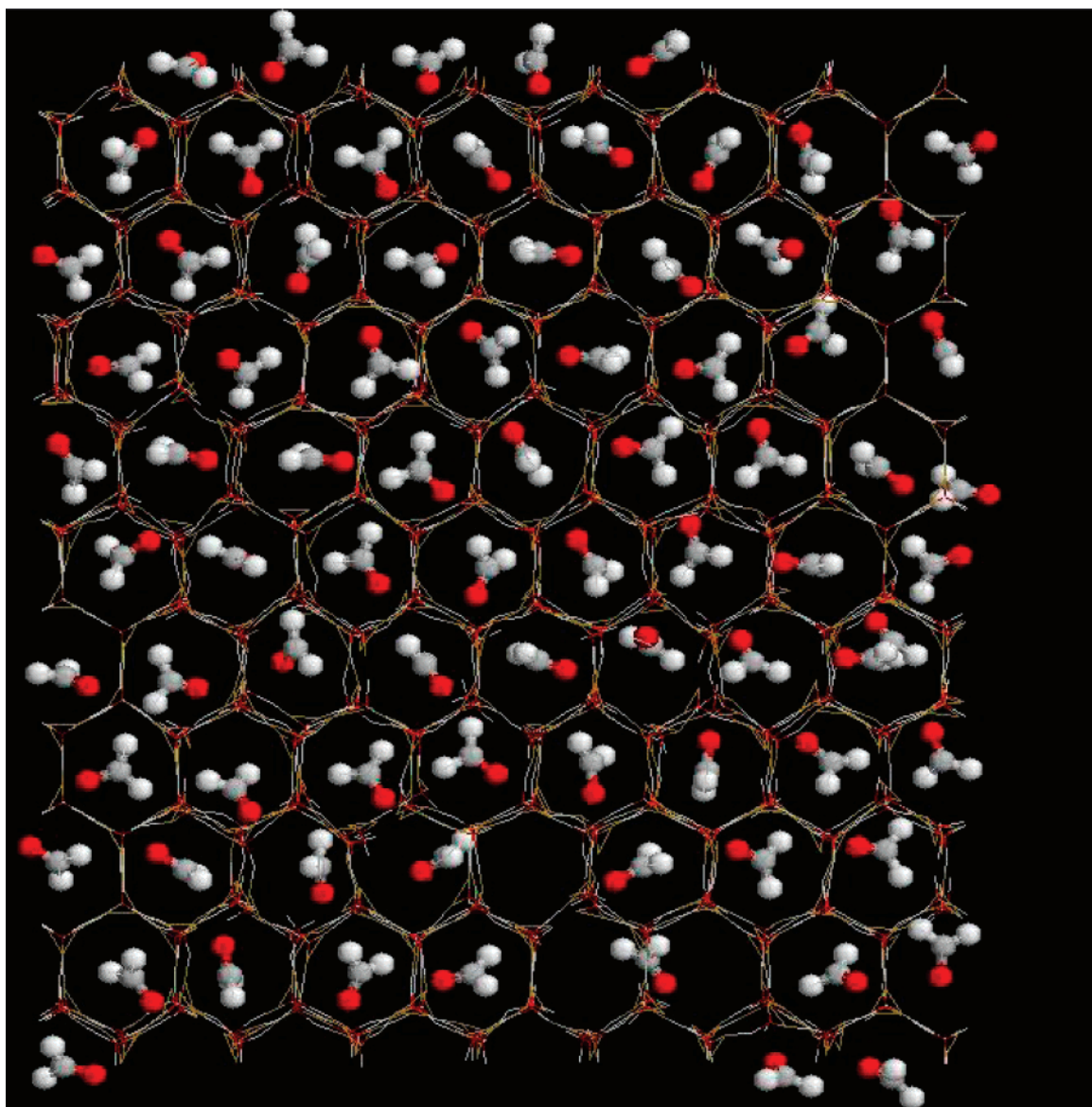


Figure 1. Top view of an instantaneous equilibrium snapshot of the $\mu = -30.01$ kJ/mol system. Water molecules are shown by sticks only; formaldehyde molecules are shown by balls and sticks. The O, C, and H atoms are shown in red, gray, and white, respectively.

where the parameters Γ_{\max} and K are the saturated surface density and Langmuir partitioning coefficient, respectively. As is seen from Figure 3, the calculated $\Gamma(p_{\text{rel}})$ points can be very well fitted by the Langmuir isotherm. This behavior is again in clear contrast to that of methanol, the adsorption of which on ice was found to be clearly of non-Langmuir nature. To illustrate this, the $\Gamma(p_{\text{rel}})$ points calculated recently for methanol³⁵ along with their best fitting Langmuir function are also shown in Figure 3 (bottom panel). Considering the facts that (i) the Langmuir adsorption isotherm is based on the neglect of the lateral interactions between the adsorbed molecules and (ii) in the case of methanol we observed strong lateral interactions (i.e., hydrogen bonding) between the neighboring molecules in the adsorption layer,³⁵ which can account for the non-Langmuir behavior of the methanol isotherm, we can conclude that the lack of the stability of the saturated formaldehyde monolayer is, at least partly, originated in the lack of considerably strong interactions between the adsorbed formaldehyde molecules.

3.2. Properties of the Adsorbed Molecules. To characterize the properties of the adsorbed layer of the formaldehyde molecules in more detail, we have performed further analyses on the collected sample configurations of two systems, char-

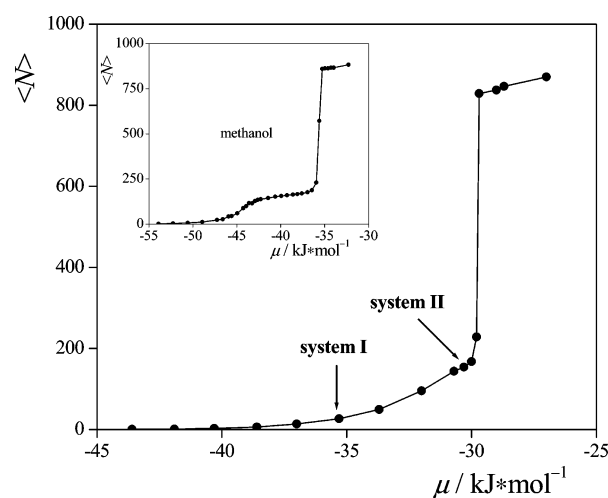


Figure 2. Average number of formaldehyde molecules in the basic simulation box as a function of the formaldehyde chemical potential. The arrows indicate the systems used in the detailed analyses. The inset shows the similar curve calculated previously for methanol molecules³⁵ for comparison.

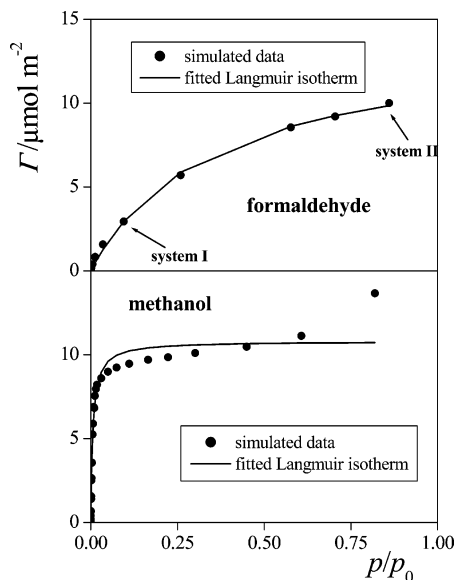


Figure 3. Adsorption isotherm of formaldehyde (top) and methanol³⁵ (bottom) on ice, as obtained from our simulation (circles), together with the Langmuir isotherm (see eq 6) fitted to these data (solid lines). The arrows indicate the systems used in the detailed analyses.

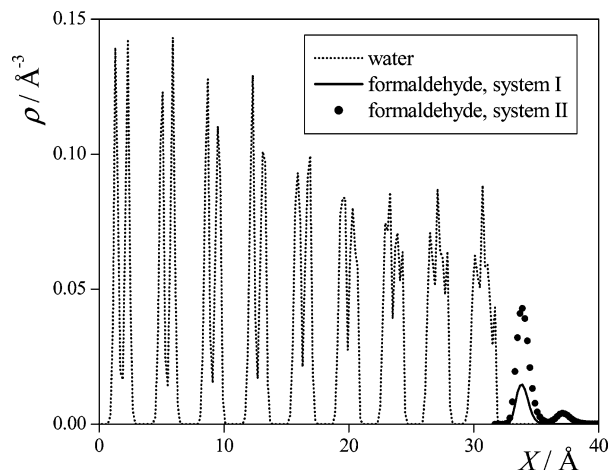


Figure 4. Molecular number density profile of water in system I (dotted line), and formaldehyde in systems I (solid line) and II (filled circles). All profiles shown are symmetrized over the two interfaces present in the basic simulation box.

acterized by the chemical potential values of -33.65 and -30.01 kJ/mol, respectively. These systems are denoted here as I and II, respectively. System I lies on the slowly rising part of the $\langle N \rangle(\mu)$ adsorption isotherm. Here the average number of the formaldehyde molecules is only about 50; thus, this system corresponds to low coverage of the ice surface. System II, containing about 170 formaldehyde molecules, is close to the point of condensation, and therefore we can expect that this system is characterized by a saturated formaldehyde monolayer. The points corresponding to these two systems on the adsorption isotherm are marked by arrows in Figures 2 and 3.

3.2.1. Density Profiles. To analyze the arrangement of the molecules along the surface normal axis X , we have calculated the density profile of both the water and the formaldehyde molecules in systems I and II. In this calculation the position of a water molecule and a formaldehyde molecule has been represented by the position of its O and its C atom, respectively. Figure 4 shows the water and formaldehyde density profiles as obtained in system I, and also the formaldehyde profile as resulted in system II. (The water density profile was found to

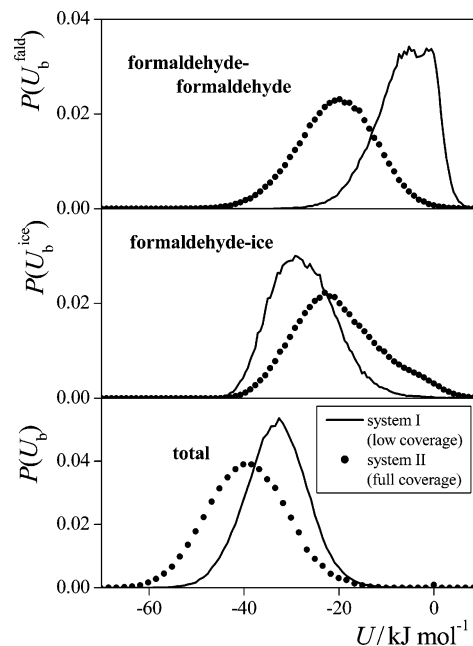


Figure 5. Distribution of the binding energy of an adsorbed formaldehyde molecule (i.e., the energy of interaction between the adsorbed molecule and the rest of the system, bottom panel), and that of its contributions coming from the interaction of the formaldehyde molecule with the ice phase (middle panel) and with the other formaldehyde molecules (top panel). Solid lines, system I; filled circles, system II.

be nearly identical in the two systems, and therefore it is only shown in the system of lower formaldehyde content.) All the profiles shown are symmetrized over the two interfaces present in the basic simulation box.

As is seen, the nine separate layers of ice can be well distinguished, even if the surface layer is noticeably broader than the layers inside the ice phase, indicating surface-induced disordering of the water molecules. In the case of $\mu = -33.65$ kJ/mol, all the formaldehyde molecules are indeed adsorbed at the surface of ice, as the density profile drops to zero beyond the X value of 35.7 Å, i.e., at the distance that is about one molecular layer away from the ice surface. In system II the majority of the formaldehyde molecules are again in contact with the ice phase; however, a second peak of the density profile appears at about $X = 37.1$ Å, indicating that after the completion of the first adsorption layer the formaldehyde molecules start to build up a second layer before their condensation occurs. The integration of the density profile reveals that about 90% of the formaldehyde molecules belong to the first adsorption layer. The formaldehyde molecules located beyond this first layer (i.e., beyond the $|X|$ value of 35.7 Å, corresponding to the minimum between the first and second density peaks) are omitted from the subsequent analyses.

3.2.2. Energetics of the Adsorption. To characterize the energetic background of the adsorption, we have evaluated the energy of the interaction of an adsorbed formaldehyde molecule (belonging to the first adsorption layer) with the rest of the system U_b , and the contributions to this binding energy that are coming from the interactions of the adsorbed molecule with the ice phase, U_b^{ice} , and with the other formaldehyde molecules present in the system, U_b^{fald} . The distribution of the U_b , U_b^{ice} , and U_b^{fald} energy terms are shown in Figure 5 as obtained in systems I and II.

At low surface coverage the dominant term of U_b comes from the interaction of the adsorbed formaldehyde molecules with the ice phase. The $P(U_b^{ice})$ distribution has its peak at

−30 kJ/mol, i.e., at only slightly larger energies than the position of the peak of $P(U_b)$ at −32.3 kJ/mol. The peak position of the $P(U_b^{\text{ice}})$ distribution suggests that the adsorbed formaldehyde molecules form a hydrogen bond with the surface waters. It should be noted that in the case of methanol adsorption the methanol molecules that are singly hydrogen bonded to the ice surface give a peak of $P(U_b^{\text{ice}})$ at a very similar energy value, i.e., −31 kJ/mol.³⁵ On the other hand, the mean value of the $P(U_b^{\text{ice}})$ distribution of −27.3 kJ/mol, which can also be regarded as an estimate of the heat of adsorption at very low surface coverages (i.e., when the formaldehyde–formaldehyde contribution to U_b is negligibly small), is nearly half of the value obtained for methanol, i.e., −49.8 kJ/mol.³⁵ This finding can be understood considering the fact that, at low surface coverages, the majority of the adsorbed methanol molecules form two hydrogen bonds with the surface waters,³⁵ whereas here the lack of a second peak of $P(U_b^{\text{ice}})$ at lower energies indicates that the adsorbed formaldehyde molecules do not participate in more than one water–formaldehyde hydrogen bond.

Upon saturation of the first adsorption layer, the peak of $P(U_b^{\text{ice}})$ moves to higher (i.e., smaller in magnitude) energies, due to the increasing competition of the adsorbed molecules for the hydrogen-bonding positions. Thus, in system II it appears only at −23 kJ/mol. This weakening of the adsorbate–water hydrogen bonds upon saturation is considerably stronger than what was observed in the case of methanol adsorption, when the peak of the adsorbed molecules singly hydrogen bonded to the ice surface was found to move to −27 kJ/mol.³⁵ However, in spite of this weakening of the interaction of the adsorbed molecules with the ice phase, the distribution of the total energy $P(U_b)$ is shifted to lower energies upon saturation. Correspondingly, the position of the peak of $P(U_b)$ moves from −32.3 kJ/mol in system I to −39.5 kJ/mol in system II. This shift is due to the increasing lateral interaction of the adsorbed molecules with increasing surface density. Thus, contrary to system I, where the $P(U_b^{\text{fald}})$ distribution has its peak between −5 and 0 kJ/mol, in system II this distribution shows a rather broad peak at −20 kJ/mol. Since the formaldehyde molecule has no H atom to be donated in strong hydrogen bonds, the dominant part of the lateral interaction is presumably of dipole–dipole type. This view is also supported by the fact that in the adsorption layer of methanol the peak of a similar distribution appears at considerably lower energies, i.e., at −32 kJ/mol.³⁵ Such a dipole–dipole type lateral interaction requires the presence of either neighboring formaldehyde molecules with oppositely oriented dipole vectors, or chains of formaldehyde molecules of parallel dipole vectors in head-to-tail type arrangements within the first adsorption layer. Both of these arrangements can be observed in the snapshot of Figure 1. To confirm the dominance of the dipole–dipole type lateral interaction of the adsorbed formaldehyde molecules, we have calculated the angle-averaged lateral dipole–dipole correlation function $\langle \cos \gamma \rangle(r_{\text{lat}})$ of the adsorbed molecules (i.e., the average cosine value of the dipole–dipole angle γ of two molecules within the first adsorption layer that are at the lateral distance r_{lat} from each other) in system II (Figure 6). This function shows a periodic oscillation, indicating that neighbors within the lateral distance of about 3.5 Å prefer antiparallel, whereas neighbors between the lateral distances of 3.5 and 6.2 Å (i.e., the boundary of the first lateral coordination shell) prefer parallel dipole–dipole orientation. To further confirm this finding, we have calculated the cosine distribution of the dipole–dipole angle γ of the neighboring molecules in the first adsorption layer that are within the lateral distances of 3.5 and 6.2 Å from each other.

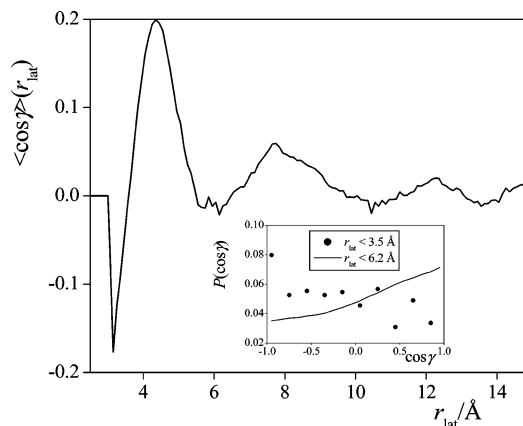


Figure 6. Angle-averaged lateral dipole–dipole correlation function of the adsorbed formaldehyde molecules in the first molecular layer of system II. The inset shows the cosine distribution of the dipole–dipole angle γ of the molecule pairs that are within the lateral distance of 3.5 Å (circles) and 6.2 Å (solid line) from each other.

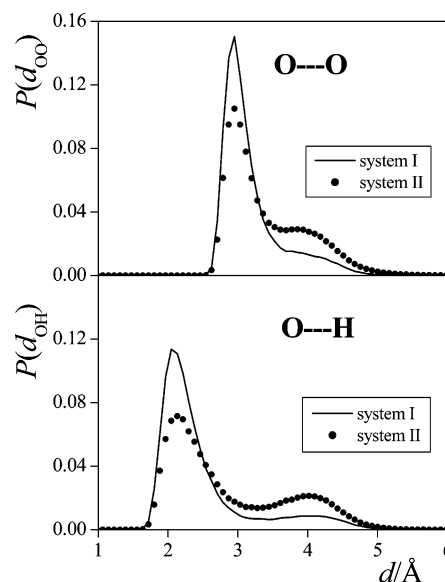


Figure 7. Distribution of the distance of the O atom of a formaldehyde molecule belonging to the first adsorption layer from the nearest water O atom (top) and from the nearest of the two H atoms of this water molecule (bottom) in systems I (solid lines) and II (filled circles).

These distributions, shown in the inset of Figure 6, are in full accordance with the above conclusions. Finally, it should be noted that although these dipole–dipole type interactions are strong enough to compensate for the weakening of the formaldehyde–ice hydrogen bonds observed with increasing surface density, they are certainly not strong enough to noticeably modify the Langmuir-like behavior of the adsorption isotherm (see Figure 3).

To analyze the geometry of the water–formaldehyde hydrogen bonds, we have calculated the distribution of the distance d_{OO} between the O atom of a formaldehyde molecule and the nearest water O atom, and that of the distance d_{OH} between the formaldehyde O and nearest water H atom in systems I and II. All the obtained distributions, shown in Figure 7, are bimodal, indicating that some of the adsorbed formaldehyde molecules do not form any hydrogen bond with water. The presence of formaldehyde molecules that are not hydrogen bonded to the ice phase in the first adsorption layer can be explained by the lateral dipole–dipole interaction of the neighboring formaldehydes. These molecules are probably evidenced in the energy distribution by the apparent asymmetry of the $P(U_b^{\text{ice}})$ distribu-

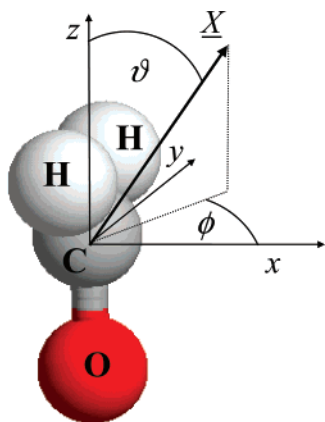


Figure 8. Definition of the local Cartesian coordinate frame fixed to the individual formaldehyde molecules in order to describe their surface orientation. \hat{X} is the surface normal vector pointing away from the ice phase; ϑ and ϕ are its polar coordinates in this molecule-fixed local frame.

tion peaks, as they give rise to the slowly decaying tail of these peaks at the high-energy side. The integration of the $P(d_{\text{OO}})$ and $P(d_{\text{OH}})$ distributions up to the minimum located between the two maxima (i.e., 3.65 Å for d_{OO} and 3.20 Å for d_{OH}) reveals that in system I about 90%, whereas in system II 70%, of the formaldehyde molecules belonging to the first adsorption layer (i.e., about 45 and 105 molecules, respectively) are hydrogen bonded to the ice phase. The positions of the first peaks of the obtained $P(d_{\text{OO}})$ and $P(d_{\text{OH}})$ distributions are found to be about 2.95 and 2.10 Å, respectively. These values are somewhat larger than the typical hydrogen-bonding $\text{O}\cdots\text{O}$ and $\text{O}\cdots\text{H}$ distances of about 2.85 and 1.9 Å, respectively, observed, e.g., in liquid water.⁴⁴

3.2.3. Orientation of the Adsorbed Formaldehyde Molecules and Hydrogen Bonding with the Surface Waters. To unambiguously describe the orientation of an adsorbed formaldehyde molecule relative to the ice surface, one has to calculate the ϑ and ϕ angular polar coordinates of the surface normal vector \hat{X} (pointing, by convention, to the vapor phase) in a molecule-fixed coordinate frame.^{45,46} Here we define this local frame in the following way. Its axis x is perpendicular to the plane of the formaldehyde molecule, axis z coincides with the main symmetry axis of the molecule (pointing from the O atom to the midpoint between the two H atoms), and axis y is perpendicular to the above two axes. In this way, ϑ is the angle formed by the interface normal vector and the main symmetry axis of the molecule, whereas ϕ is the angle between the molecular normal vector and the projection of the interface normal vector to the plane that is perpendicular to the main symmetry axis of the formaldehyde molecule. The definition of this local frame and of the polar angles ϑ and ϕ is illustrated in Figure 8.

The orientational statistics of the formaldehyde molecules relative to the ice surface can fully be described by calculating the bivariate distribution of the angular variables ϑ and ϕ . However, considering the fact that ϑ is formed by two general spatial vectors but ϕ is the angle of two vectors that are restricted to lie in a given plane by definition, uncorrelated orientation of the molecules with the ice surface will only result in a uniform bivariate distribution if $\cos \vartheta$ and ϕ are used as independent variables.^{45,46}

The $P(\cos \vartheta, \phi)$ orientational maps of the adsorbed formaldehyde molecules are shown in Figure 9 as obtained in systems I and II. As is seen, in system I the orientational map exhibits one single maximum at the $\{\cos \vartheta = 0.2; \phi = 0^\circ\}$ point. This

point, denoted by “A”, corresponds to the orientation in which the formaldehyde molecule lies nearly parallel with the ice surface, its main axis of symmetry declines only by about 15° from the plane of the surface, and the two H atoms are at equal distance from the surface. This orientation, illustrated also in Figure 9, is in good agreement both with the results of our earlier molecular dynamics simulation²¹ and with the ab initio calculations of Marinelli and Allouche.²⁰ The orientation map obtained in system II has its maximum at the same $\cos \vartheta$ value as that obtained in system I (i.e., at 0.2), but at $\phi = 90^\circ$ instead of $\phi = 0^\circ$. This orientation, denoted by “B”, can be obtained from orientation A through a 90° rotation of the formaldehyde molecule around its main axis of symmetry. Thus, in this orientation the plane of the formaldehyde molecule is perpendicular to the ice surface, as demonstrated in Figure 9.

The orientation of the water molecules at the surface of I_h ice is such that their O–H bonds can point to the vapor phase either flatly, declining by about $15\text{--}20^\circ$ from the surface (this alignment of the O–H bond can correspond to two possible water orientations), or straight, being perpendicular to the surface (see, e.g., Figure 9 of ref 35). Considering the facts that, due to its sp^2 hybrid state, the two lone pair directions of the O atom of the formaldehyde molecule (i.e., the two directions in which the molecule can accept a hydrogen bond) are lying in the plane of the molecule, and that in its preferred orientation A the plane of the formaldehyde molecule is nearly parallel with the ice surface, we can conclude that in this orientation the formaldehyde molecule can only accept the hydrogens of the flat O–H bonds of the surface water molecules. On the other hand, in orientation B the plane of the formaldehyde is perpendicular to the ice surface; hence one of the lone pair directions of its O atom points nearly straight to the ice phase, declining by about $15\text{--}20^\circ$ from the direction of the surface normal. (The other lone pair direction points to the vapor phase.) Therefore, in this orientation the formaldehyde molecule can form a hydrogen bond with a water O–H bond that is perpendicular to the surface and sticks straight to the vapor phase. However, the aforementioned $15\text{--}20^\circ$ deviation between the formaldehyde lone pair and water O–H directions leads to some distortion of the geometry of these bonds, resulting in the fact that the adsorbed formaldehyde molecules were found to form relatively weak hydrogen bonds with the ice surface in system II (see Figure 5). The relative arrangements of the above two possible water–formaldehyde pairs, in which both participating molecules are in one of their preferred alignments relative to the ice surface, are shown in Figure 10.

The obtained results clearly show that the thermodynamic driving force of the adsorption of the formaldehyde molecules is the possibility of forming hydrogen bonds with the surface water molecules. At low surface coverage the formaldehyde molecules prefer to orient in such a way that they can form a strong hydrogen bond with the surface waters. However, in the case of the saturated adsorption monolayer the free energy of the system can be minimized by maximizing the number of the water–formaldehyde hydrogen bonds per surface unit. This requirement can be fulfilled if the water–formaldehyde hydrogen bonds align perpendicular to the ice surface, leading to the observed flipping over of the preferred formaldehyde orientation upon saturation, and to the observed distortion and weakening of the water–formaldehyde hydrogen bonds. Further, in orientation B not only the surface area occupied by a water–formaldehyde hydrogen bond is minimal (since it stays perpendicular to the surface), but also the surface area occupied by a formaldehyde molecule, which stays perpendicular to the surface, is considerably smaller than in orientation A, when it

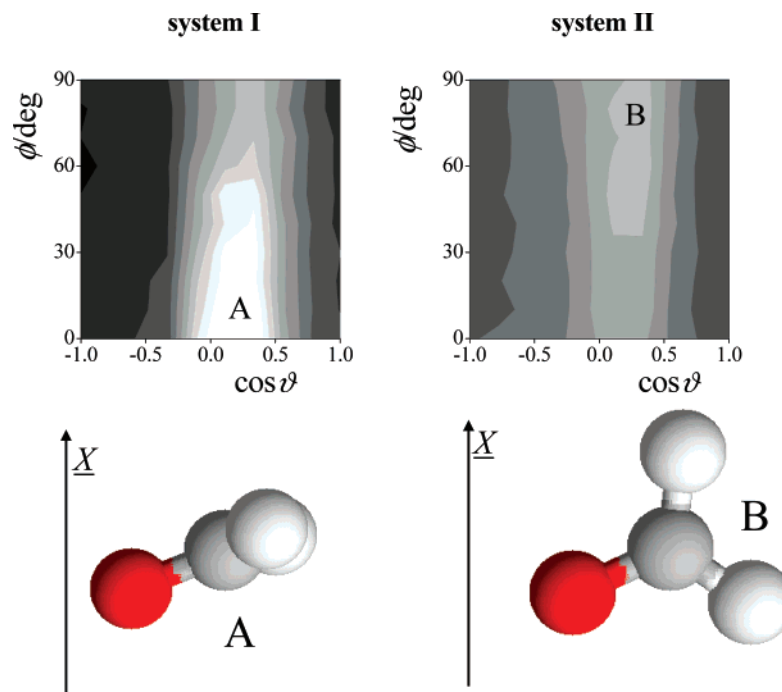


Figure 9. Orientational map of the formaldehyde molecules adsorbed at the ice surface in system I (left) and in system II (right). Lighter colors indicate higher probabilities. The formaldehyde orientations corresponding to peaks A and B of the orientational maps are also indicated. \underline{X} is the surface normal vector pointing away from the ice phase.

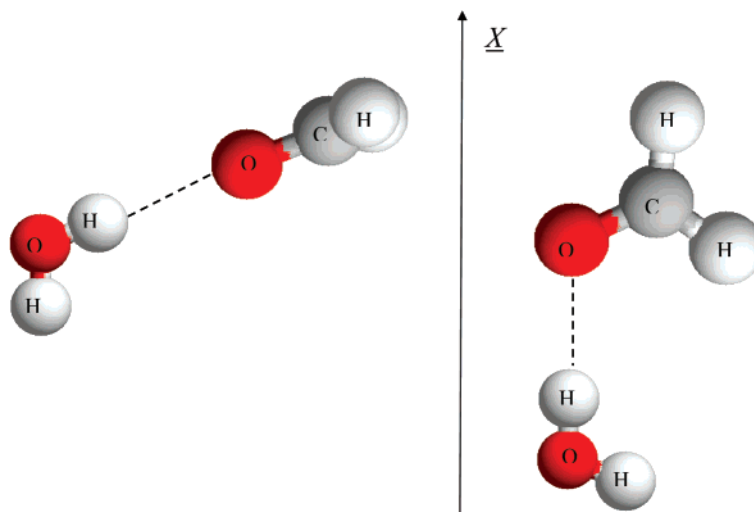


Figure 10. Possible hydrogen bonds between a water molecule located at the ice surface and an adsorbed formaldehyde molecule aligned in one of the preferred orientations. Left, formaldehyde is in orientation A; right, formaldehyde is in orientation B. \underline{X} is the surface normal vector pointing away from the ice phase.

lies almost parallel with the surface. In addition to the possibility of the formation of water–formaldehyde hydrogen bonds, the lateral, dipole–dipole type interactions also give some contribution to the thermodynamic driving force of the adsorption, although this contribution is certainly too small to noticeably alter the Langmuir-type adsorption behavior of formaldehyde. It should be noted that the dipole vector of the adsorbed formaldehyde molecules is nearly parallel with the ice surface in both of their preferred orientations, which makes strong dipole–dipole pairing of the neighboring formaldehyde molecules rather easy within the first adsorption layer.

4. Summary and Conclusions

In this paper we have presented the calculation of the adsorption isotherm of formaldehyde at the surface of I_h ice. In light of the obtained results, we can interpret the experimentally

observed differences¹¹ between the adsorption processes of formaldehyde and methanol. The most important difference is that the formaldehyde molecules can only establish much weaker (dipole–dipole type) lateral interactions with each other than the methanol molecules, which form, on average, one hydrogen bond with another methanol in their saturated monolayer.³⁵ Due to the lack of strong lateral interactions, the adsorption of the formaldehyde molecules, unlike that of methanol, exhibits a purely Langmuir-like behavior.

The main driving force of the formaldehyde adsorption is found to be the formation of hydrogen bonds with the surface water molecules. Although the possibility of the formation of such water–adsorbate hydrogen bonds is also the most important factor that is responsible for the adsorption of the methanol molecules, there are several important differences between the two processes also in this respect. Thus, first of all, in the case

of low surface coverage the vast majority of the methanol molecules participate in two hydrogen bonds with the surface water molecules. Further, even in the case of the saturated methanol monolayer, about half of the methanol molecules form two hydrogen bonds with waters.³⁵ On the other hand, the formaldehyde molecules never form more than one hydrogen bond with the ice phase. Finally, the hydrogen bonds formed by the formaldehyde molecules of their saturated monolayer with the interfacial waters are found to be somewhat weaker than those between the adsorbed methanol and surface water molecules. All these factors (i.e., the lack of lateral hydrogen bonding, fewer and weaker water–adsorbate hydrogen bonds) together result in the fact that the thermodynamic driving force (i.e., the accompanying free energy gain) of the adsorption of formaldehyde is much weaker than that of the adsorption of methanol. This fact can explain also the experimental observation that, contrary to methanol, no temperature dependence of the adsorption isotherm of formaldehyde can be detected at low pressures.¹¹ Since such a temperature dependence is related to the enthalpy of adsorption, this experimental observation can simply be explained with the considerably smaller heat of adsorption of formaldehyde than that of methanol, in accordance also with the estimates made on the basis of our simulation.

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References and Notes

- (1) Singh, H. B.; Kanakidou, M.; Crutzen, P. J.; Jacob, D. J. *Nature* **1995**, *378*, 50.
- (2) Sumner, A. L.; Shepson, P. B. *Nature* **1999**, *398*, 230.
- (3) Honrath, R. E.; Peterson, M. C.; Guo, S.; Dibbs, J. E.; Shepson, P. B.; Campbell, B. *Geophys. Res. Lett.* **1999**, *26*, 695.
- (4) Jones, A. E.; Weller, R.; Anderson, P. S.; Jacobi, H. W.; Wol., E. W.; Schrems, O.; Miller, H. *Geophys. Res. Lett.* **2001**, *28*, 1499.
- (5) Hutterli, M. A.; Rothlisberger, R.; Bales, R. C. *Geophys. Res. Lett.* **1999**, *26*, 1691.
- (6) Hutterli, M. A.; Bales, R. C.; McConnell, J. R.; Stewart, R. W. *Geophys. Res. Lett.* **2002**, *29*, 1029.
- (7) Jacobi, H. W.; Frey, M. M.; Hutterli, M. A.; Bales, R. C.; Schrems, O.; Cullen, N. J.; Steffen, K.; Koehler, C. *Atmos. Environ.* **2002**, *36*, 2619.
- (8) Perrier, S.; Houdier, S.; Domine, F.; Cabanes, A.; Legagneux, L.; Sumner, A. L.; Shepson, P. B. *Atmos. Environ.* **2002**, *36*, 2695.
- (9) Burkhart, J. F.; Hutterli, M. A.; Bales, R. C. *Atmos. Environ.* **2002**, *36*, 2157.
- (10) Perrier, S.; Sassin, P.; Domine, F. *Can. J. Phys.* **2003**, *81*, 319.
- (11) Winkler, A. K.; Holmes, N. S.; Crowley, J. N. *Phys. Chem. Chem. Phys.* **2002**, *4*, 5270.
- (12) Sokolov, O.; Abbatt, J. P. D. *J. Phys. Chem. A* **2002**, *106*, 775.
- (13) Domine, F.; Rey-Hanot, L. *Geophys. Res. Lett.* **2002**, *29*, 1873.
- (14) Hudson, P. K.; Zondlo, M. A.; Tolbert, M. A. *J. Phys. Chem. A* **2002**, *106*, 2882.
- (15) Abbatt, J. P. D. *Chem. Rev.* **2003**, *103*, 4783.
- (16) Bartels-Rausch, T.; Guimbaud, C.; Gäggeler, H. W.; Ammann, M. *Geophys. Res. Lett.* **2004**, *31*, L16110.
- (17) Peybernès, N.; Marchand, C.; Le Calvé, S.; Mirabel, P. *Phys. Chem. Chem. Phys.* **2004**, *6*, 1277.
- (18) Picaud, S.; Hoang, P. N. M.; Peybernès, N.; Le Calvé, S.; Mirabel, P. *J. Chem. Phys.* **2005**, *122*, 194707.
- (19) Picaud, S.; Hoang, P. N. M. *J. Chem. Phys.* **2000**, *112*, 9898.
- (20) Marinelli, F.; Allouche, A. *Chem. Phys.* **2001**, *272*, 137.
- (21) Collignon, B.; Picaud, S. *Chem. Phys. Lett.* **2004**, *393*, 457.
- (22) Peybernès, N.; Le Calvé, S.; Mirabel, P.; Picaud, S.; Hoang, P. N. M. *J. Phys. Chem. B* **2004**, *108*, 17425.
- (23) Ballenegger, V.; Picaud, S.; Toubin, C. *Chem. Phys. Lett.* **2006**, *432*, 78.
- (24) Pártay, L. B.; Jedlovsky, P.; Hoang, P. N. M.; Picaud, S.; Mezei, M. *J. Phys. Chem. C* **2007**, *111*, 9407.
- (25) Adams, D. J. *Mol. Phys.* **1975**, *29*, 307.
- (26) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Clarendon Press: Oxford, 1987.
- (27) Muller, E. A.; Rull, L. F.; Vega, L. F.; Gubbins, K. E. *J. Phys. Chem.* **1996**, *100*, 1189.
- (28) Muller, E. A.; Gubbins, K. E. *Carbon* **1998**, *36*, 1433.
- (29) Muller, E. A.; Hung, F. R.; Gubbins, K. E. *Langmuir* **2000**, *16*, 5418.
- (30) Brennan, J. K.; Bandosz, T. J.; Thomson, K. T.; Gubbins, K. E. *Colloids Surf., A* **2001**, *187–188*, 539.
- (31) Stirolo, A.; Chialvo, A. A.; Gubbins, K. E.; Cummings, P. T. *J. Chem. Phys.* **2005**, *122*, 234712.
- (32) Moulin, F.; Picaud, S.; Hoang, P. N. M.; Pártay, L.; Jedlovsky, P. *Mol. Simul.* **2006**, *32*, 487.
- (33) Puibasset, J.; Pellenq, R. J. M. *J. Chem. Phys.* **2003**, *118*, 5613.
- (34) Puibasset, J.; Pellenq, R. J. M. *J. Chem. Phys.* **2005**, *122*, 094704.
- (35) Jedlovsky, P.; Pártay, L.; Hoang, P. N. M.; Picaud, S.; von Hessberg, P.; Crowley, J. N. *J. Am. Chem. Soc.* **2006**, *128*, 15300.
- (36) Mahoney, M.; Jorgensen, W. L. *J. Chem. Phys.* **2000**, *112*, 8910.
- (37) Jorgensen, W. L.; Maxwell, D. S.; Tirado-Rives, J. *J. Am. Chem. Soc.* **1996**, *118*, 11225.
- (38) Mezei, M. *MMC: Monte Carlo program for simulation of molecular assemblies*. URL: <http://inka.mssm.edu/~mezei/mmc>.
- (39) Barker, J. A.; Watts, R. O. *Mol. Phys.* **1973**, *26*, 789.
- (40) Neumann, M. *J. Chem. Phys.* **1985**, *82*, 5663.
- (41) Mezei, M. *Mol. Phys.* **1980**, *40*, 901.
- (42) Mezei, M. *Mol. Phys.* **1987**, *61*, 565; Erratum: *Mol. Phys.* **1989**, *67*, 1207.
- (43) Daub, C. D.; Patey, G. N.; Jack, D. B.; Sallabi, A. K. *J. Chem. Phys.* **2006**, *124*, 114706.
- (44) Soper, A. K.; Phillips, M. G. *Chem. Phys.* **1986**, *107*, 47.
- (45) Jedlovsky, P.; Vincze, Á.; Horvai, G. *J. Chem. Phys.* **2002**, *117*, 2271.
- (46) Jedlovsky, P.; Vincze, Á.; Horvai, G. *Phys. Chem. Chem. Phys.* **2004**, *6*, 1874.