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Molecular-scale simulations of organic compounds on ice: application to atmospheric and interstellar sciences.

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Molecular-scale simulations of organic molecules adsorbed on ice: application to atmospheric and interstellar sciences.

In this paper, we present a brief review of what has been learned about the adsorption characteristics of various organic molecules at the surface of ice, from more than 15 years of computer simulation studies at the molecular scale. In particular, grand canonical Monte Carlo and molecular dynamics calculations were performed to determine the adsorption isotherms, the saturation coverage of the first molecular layer at the ice surface, the preferred orientations of the molecules in their adsorption sites, and the corresponding adsorption energies. The results of the simulations indicated that the main driving force for trace gas adsorption on ice is hydrogen bonding not only between the adsorbate and the water molecules of the ice surface, but also within the adsorbate. When possible, the comparison with available experimental data showed a close agreement, supporting thus the methodology used in the modelling. Finally, the present review demonstrates how computer simulation can nicely complement experimental approaches for studying interactions between trace gases and ice under tropospheric and interstellar condition

Keywords: ice, adsorption, trace gases, simulation, molecular dynamics, Monte Carlo

1. Introduction

Water is present everywhere in the Universe, from the solar system to interstellar medium and its search in, *i.e.*, exoplanets is considered as a critical test for exobiology [1]. Because of the low temperatures of these regions, water can often be found in the solid state, *i.e.*, exhibiting amorphous or crystalline forms of ice [2]. The existence of clathrate hydrates has also been postulated, when the thermodynamics conditions are favourable to their formation [3].

In the solar system, these different forms of water ice have long been recognised in the outer planets and comets, and are also observed throughout the terrestrial planet region [4]. Two main reservoirs of ices are invoked by formation scenarios of the

protoplanetary nebula to explain the presence of icy-bodies in the solar system. The first reservoir, located within 30 Astronomical Units (AU) of the Sun, contains mostly crystalline water ice whereas the other one, located at larger heliocentric distances, is composed of amorphous ice originating from ISM that did not vaporize/recrystallize when entering into the disk [5].

On Earth, ice occurs in many forms, such as micrometer-sized particles in cirrus clouds, snowflakes, hailstones in the atmosphere, and, on the ground, as snow, firn, glacial and sea ice [6]. The large snow-covered areas play a fundamental role in controlling the Earth's climate due to their strong albedo [7]. Ice and snow can also efficiently scavenge and accumulate compounds of environmental concern playing, thus, an integral role in transferring trace gases to and from the atmosphere [8]. Ice particles constituting polar stratospheric clouds (PSCs) have been recognized to help at converting "reservoir" species of chlorine over to more photochemically active forms that, finally, lead to a seasonal ozone depletion (the so-called "Ozone hole") [9]. At the cold temperatures of the upper troposphere, cirrus ice clouds are widely prevalent, promoting reactive heterogeneous chemistry and scavenging semivolatile gas-phase species [10].

On the other hand, interstellar and cometary dust grains are frequently covered by amorphous solid water that may trap volatile species and act both as a catalyst and as a chemical reactant [11]. Indeed, water ice in interstellar medium or comets is subject to, *e.g.*, cosmic rays, UV irradiation and thermal reactions, which initiate a rich solid-state chemistry that may ultimately lead to the formation of new and more complex molecules [12,13].

A thorough characterization of the trace gas uptake processes on ice is thus of fundamental interest to adequately assess the environmental fate of many atmospheric

species and better predicting climate's evolution [14]. The detailed investigation of the interactions between various organic molecules and amorphous ice surfaces, as well as the characterization of clathrate hydrates stability, are also crucial for understanding the fate of interstellar molecules, in connection with the possible delivery to early Earth of prebiotic molecules sequestered with a protective water ice host, and with the possible emergence of Earth-like life elsewhere in the universe [15].

The adsorption of trace gases on ice surfaces has thus been widely characterized experimentally in the past decades [6,8,10,16,17], especially in the environmental context [18]. Similarly, interactions of gaseous species with interstellar ices [19,20] as well as the trapping of various molecules in clathrate hydrates [21] have been extensively investigated in laboratory.

However, despite these experimental investigations, fundamental questions regarding the details of the adsorption/interaction processes remain unanswered, such as where the trapped molecules prefer to locate at the ice surface, how do they bind to the water molecules, how many hydrogen bonds do they form with ice, and how the competition between these hydrogen bonds and lateral hydrogen-bonding between adsorbed species may favor the formation of structured adlayer(s) on ice. These points can be tackled at a theoretical level by means of atomistic simulations. Indeed, given that the chosen model accurately reproduces experimentally known properties of the investigated systems, computer simulations can provide detailed direct insights into the structure, energetic and dynamics of the studied system on the molecular level [22,23].

Thus, for more than 15 years, we have developed numerical simulations to investigate the adsorption of trace gases, especially organic molecules, on ice surfaces under tropospheric, and more recently, interstellar, conditions. Then, in a series of previous papers, we used molecular dynamics (MD) and/or Monte-Carlo (MC)

simulations to model, at the molecular scale, the interaction between ice and various alcohols (methanol [24,25], ethanol [26]), aldehydes (formaldehyde [24,27], acetaldehyde [28], benzaldehyde [29]), carboxylic acids (formic [30,31], acetic [32], oxalic [33] acids), ketones (acetone [34,35], hydroxyacetone [36]), aromatic molecules (benzene [37], naphthalene [37], anthracene [37], phenanthrene [37,38], benzaldehyde [29]), halogenated methane derivatives [39-43], methylamine [44,45], hydrogen peroxide [46], and hydrogen cyanide [47]. We also simulated the trapping of various atomic and molecular species into clathrate hydrates in the astrophysical context [48-50]. In these simulations, calculations have taken a large number of molecules into account and have included temperature effects, in contrast with, *e.g.*, optimization methods that are usually restricted to a limited number of molecules the adsorption of which being investigated at 0 K.

In these studies, the Grand Canonical Monte Carlo (GCMC) method has been shown to be a particularly suitable tool to simulate adsorption experiments on ice because it allows the theoretical determination of the adsorption isotherm, *i.e.*, the surface coverage as a function of the partial pressure at a given temperature. Indeed, by systematically varying the chemical potential (μ) of the adsorbate, the mean number of adsorbed molecules can be determined as a function of μ at a given temperature. Furthermore, MD simulations have allowed the determination of dynamics quantities, such as the surface and bulk diffusion coefficients [51]. Finally, because adsorption processes are initially governed by molecular transport from the gas phase to the surface layers of ice, constrained MD [30,39] or MC simulations coupled to the Cavity Insertion Widom (CIW) method [52] have also been used to calculate the solvation free energy of various molecules including organic compounds of atmospheric interest (namely,

methanol, formaldehyde, formic and acetic acids, acetone, chloroform) across the ice/vapor interface.

Here, we present a review of the results obtained during the last 15 years on the simulation of organic compounds adsorbed on ice surfaces. We compare them with available experimental results and show that MD and MC simulations are accurate and useful tools for studying interactions between trace gases and ice under tropospheric or interstellar conditions. We intend to demonstrate that combining experimental methods with computer simulations is of great interest because the simulation results can provide deeper insight into the adsorption process than any experiment can do, whereas the comparison with experimental data allows verifying the relevance of the theoretical approaches. We also show the strong dependence of the adsorption characteristics to the functional chemical group of the organic compound under consideration.

This review paper is organized as follows. In section 2 details of the calculations are given. The results of the simulations for the various organic compounds considered are presented and discussed in section 3. Finally, in section 4 the main conclusions of this study are summarized.

2. Details of the computer simulations at the molecular scale

2.1. Modeling the ice surface

Interaction of organic compounds with the (0001) basal plane of proton ordered and proton disordered hexagonal ice has been investigated to characterize the behaviour of trace gases in the troposphere. Infinite ice surfaces have been modeled by a periodic replication of the simulation box along two directions perpendicular to the c axis of ice. This simulation box has been defined as a parallelepiped containing ten ice bilayers of 160 water molecules each, defining thus a thick ice slab. In the MD studies, this ice slab

has been located at the bottom of the simulation box, and consisted of 6 (respectively 8) bilayers of moving molecules, placed on 4 (respectively 2) bilayers of fixed molecules. In this case, adsorption has been considered on the moving gas/ice interface only. By contrast, in GCMC simulations, the ice slab has been placed in the middle of the simulation box along the c axis of ice. It has usually consisted of 18 molecular layers of proton-disordered I_h ice, containing 160 water molecules per layer, forming a perfect ice I_h crystal at the beginning of the simulations. The molecules belonging to the two innermost layers have been kept fixed during the simulations to stabilize the bulk phase of the ice crystal. In this case, adsorption was considered at the two gas/ice interfaces present in the simulation box to ensure better statistics especially at the very low values of μ for which the number of adsorbed molecules has been shown to be very weak. The initial configuration of the water molecules obeyed the ice rules and the MD box had no net charge and no net dipole moment [53].

In addition, to investigate adsorption in interstellar conditions, simulations have also been performed by considering the low density amorphous (LDA) ice phase. To create a LDA surface in the simulation box, we started from the crystalline I_h ice phase used in our other works (see above) which was then melted by heating it to 350 K, performing 3×10^8 MC steps on the canonical (N,V,T) ensemble, and then cooling it down to 300 K with another 10^8 MC steps of simulation. The melted system has been then quenched by setting the temperature to 200 K, and performing additional 10^8 Monte Carlo steps.

The water molecules have been described either by rigid three (SPC/E [54]), four (TIP4P [55]) or five-site (TIP5P [56]) models, depending on the systems under investigation. However, most often, the TIP5P model [56] has been used, because it reproduces the melting temperature of I_h ice within a few Kelvin [57]. This model

includes two non-atomic charged sites in the direction of the lone pairs of the O atom, in addition to the three atomic sites.

2.2. Modeling the interactions between trace gases and ice

To calculate the interactions between organic compounds, simple intermolecular potentials, based on site-site electrostatic and dispersion-repulsion contributions have been used. The parameters of the corresponding models have been taken from various standard force fields (OPLS-AA [58], AMBER [59], TraPPE [60]) depending on the molecules under consideration. In some situations, specifically parametrized available models such as the four-site KBFF acetone model [61] or the five-site Jedlovszky-Turi model [62] for formic acid, have also been used, since these interaction potentials have proven to provide more reliable description of the corresponding molecular properties [61,62].

Cross interactions between water and the organic molecules have been calculated using the usual Lorentz-Berthelot combining rules [63]. All interactions have been truncated using either a simple cut-off or the Ewald summation method for long-range corrections, in accordance with the original parameterization of the corresponding models. We have also shown that the treatment of the long-range part of the electrostatic interaction has rather little influence on the adsorption isotherm [34]. All details of the interaction potential models can be found in the original publications.

2.3. MD simulations

In the MD calculations, the simulation box also contained a certain number of moving organic compounds, randomly distributed above the ice surface at the beginning of the simulation. Then, the determination of the saturation coverage of the ice surface by the

molecules under consideration has been achieved by performing different simulation runs with increasing number of adsorbed molecules in the simulation box. Each molecule has been treated as a rigid rotor, with six external coordinates used to describe the translation $\{x,y,z\}$ of the center of mass, and the orientation $\{\theta,\phi,\chi\}$ of the molecule with respect to an absolute frame tied to the bottom of the simulation box. However, to account for the possible internal rotations that could be induced by the interaction with the ice surface for the large oxalic acid [33] and hydroxyacetone [36] molecules, only the atomic translational degrees of freedom have been considered in the corresponding simulations, with constraints keeping the various bond lengths unchanged but allowing bond angles and torsional flexibilities. This has been achieved by using the LINCS algorithm [64].

The equations of motions have been solved using the Verlet algorithm for translations and the quaternion representation of the molecular orientations [63]. A time step of 2.2 fs has been usually used, and each run has consisted of a long equilibration phase (typically several hundred of ps) followed by a production phase during which all the simulation data have been collected for further analysis. The initial velocities for each moving molecule have been taken from the Boltzmann distribution corresponding to the desired simulation temperature. At the beginning of the simulation, *i.e.*, during the first 25 % of the equilibration period, the temperature has been slowly increased up to the desired temperature and then, during the production run, this temperature has been kept constant using the Berendsen thermostat on the (N,V,T) ensemble [63].

2.4. GCMC simulations

Monte Carlo simulation on the grand canonical (μ,V,T) ensemble is a particularly suitable tool for calculating adsorption isotherms on ice by controlling the chemical

potential and, thus, the partial pressure, of the adsorbed molecules. Therefore, series of GCMC simulations have been performed at 200 K, *i.e.*, a temperature relevant for the upper troposphere, for various trace gases [25,27-29,31,35,37,40-43,44,46,47], aiming at comparing their ability to bind to the ice surface. Lower temperatures down to 20 K, typical of the interstellar medium, have also been considered in the case of methylamine adsorbed on amorphous ice [45], to characterize the behaviour of this precursor of glycine, an amino acid, which is of particular interest in astrochemical research because it is related to the formation of prebiotic molecules [15].

In the GCMC simulations, configurations of the systems have been generated via a set of trial moves where the standard Metropolis criteria have been used for molecule displacements, while the following acceptance probability has been applied for insertion and deletion of molecules [63]:

$$P_{acc}(N_a \rightarrow N_a + 1) = \min \left\{ 1, \frac{V}{\Lambda^3(N_a+1)} \exp\left(-\frac{(\Delta U - \mu)}{k_B T}\right) \right\} \quad (1)$$

and

$$P_{acc}(N_a \rightarrow N_a - 1) = \min \left\{ 1, \frac{\Lambda^3 N_a}{V} \exp\left(-\frac{(\Delta U + \mu)}{k_B T}\right) \right\} \quad (2)$$

where ΔU is the energy change upon the insertion or deletion move, N_a and V are the number of molecules and volume, respectively. T is the temperature, k_B is the Boltzmann constant, whereas Λ denotes the thermal de Broglie wavelength, defined as :

$$\Lambda = \frac{h}{\sqrt{2\pi k_B T m}} \quad (3)$$

where m is the mass of the molecule under consideration and h is the Planck constant.

Thus, in the GCMC simulations, the number of adsorbed molecules has been left to fluctuate around the equilibrium value corresponding to the chosen chemical potential of the organic compound in the system.

To perform these simulations we made use of the MMC code [65], in which the value of μ is controlled through the B parameter of Adams [66], related to μ through the equation [63]

$$\mu = k_B T \left(B + \ln \frac{A^3}{V} \right) \quad (4)$$

Simulations have thus been performed at constant B , V , and T , which is completely equivalent with using the (μ, V, T) ensemble. They have been repeated for various B values, to simulate adsorption isotherms from vanishingly small surface coverage to the condensation of the adsorbate in the simulation box.

In the Monte Carlo simulations, particle displacement and insertion/deletion moves have been performed with equal probabilities. In a displacement move, a randomly chosen organic or water molecule has been randomly translated by no more than 0.25 Å and randomly rotated by no more than 15°. Only the organic molecules have been inserted or deleted, with 50 % - 50 % probabilities, in the simulation box. In this procedure, insertions have been attempted at the centres of empty cavities that have been searched for along a $100 \times 100 \times 100$ grid, which has been regenerated after every 10^6 Monte Carlo steps. To remove the bias introduced into the sampling by attempting insertions solely into suitably large cavities, we made use of the cavity biased scheme of Mezei, in which the acceptance criterion of the insertion/deletion moves has been corrected by the factor of $\ln P_{cav}^N$, where P_{cav}^N is the probability of finding a suitable cavity in the system containing N adsorbed molecules [67,68].

We carefully checked in each system the number of Monte Carlo moves needed to reach equilibrium, and usually performed a minimum of 10^8 MC moves in the equilibration stage, followed by an additional 2×10^8 MC moves, during which the

properties of interest have been calculated by averaging over thousands of sample configurations.

3. Simulation Results

3.1. Adsorption of simple organic molecules on crystalline ice

Among the various molecules considered in our simulation studies, the simplest alcohol, aldehyde, ketone and carboxylic acid molecules (*i.e.*, methanol, formaldehyde, acetone and formic acid, respectively) have been characterized both by MD and GCMC simulations [24,25,27,30,31,34,35], and the theoretical results have been compared with available experimental data. For these molecules, the possible formation of a complete monolayer at the ice surface has been investigated, the adsorption energy has been determined, and the details of the hydrogen bonding at the surface have been characterized.

Because it is the first system we have fully characterized in both MD [24] and GCMC [25] simulations, let us first detail the main properties of methanol adsorbed on proton disordered I_h ice. The corresponding adsorption isotherm, $\langle N \rangle(\mu)$, is shown in Fig. 1a, as obtained from the GCMC simulations at 200 K [25]. At low μ values, this isotherm exhibits an exponential increase (up to about $\mu = -43 \text{ kJ mol}^{-1}$) that corresponds to the building up of the adsorption layer. Then, large changes in the values of μ result only in a rather small increase of the number of the adsorbed methanol molecules, which is a strong indication for the saturation of the adsorption layer. Moreover, the number of the adsorbed molecules found at this plateau region of the isotherm indicates that the saturated adsorption layer is probably monomolecular [25], in accordance with the results obtained by MD simulation at 210 K [24]. Finally, above the μ value of about $-35.5 \text{ kJ mol}^{-1}$, at which a sudden jump is evidenced in the

isotherm, methanol is present in a condensed state, filling thus the entire simulation box. To go further in our analysis, the adsorption isotherm has been converted to the $\Gamma(p_{rel})$ form, where Γ is the surface density of the methanol molecules at the ice surface, calculated as

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

where $\langle N \rangle$ is the mean number of adsorbed molecules and S is the exposed ice surface. The factor 2 in the denominator takes into account the fact that there are two gas/ice interfaces in the basic simulation box. The relative pressure $p_{rel} = p/p_0$ is the pressure of the vapor phase, p , normalized by the pressure of the saturated vapor of methanol, p_0 . It has been calculated by using the relation [69]:

$$p_{rel} = \frac{p}{p_0} = \frac{e^B}{e^{B_0}} \quad (6)$$

in which B_0 is the B value at which the condensation of methanol occurs in the simulation. This relation is only valid in the vapor phase and, as a consequence, the $\Gamma(p_{rel})$ isotherm has only been calculated up to the point of condensation (Fig.1b). An attempt to fit this isotherm by the Langmuir form (solid line in Fig. 1b) clearly indicates that methanol adsorption on ice is of non-Langmuir nature, especially at high pressure, where the number of adsorbed molecules is sufficiently high that the lateral hydrogen-bonding between methanol molecules starts to be significant, as confirmed by the analysis of the MD [24] and GCMC [25] results. Indeed, radial pair distribution functions of the distances between the H and O atoms of different molecules at the methanol/ice interface, as calculated in MD simulations at 210 K, exhibit a strong peak centered around 2.0 Å that corresponds to the typical distance of a H-bond [24]. This peak has been observed in all the pair distribution functions between O and H atoms of the methanol hydroxyl group and H and O atoms of water, as well as between O and H

atoms of neighbouring methanol hydroxyl groups, indicating that the methanol molecules can act both as proton donor and proton acceptor in their hydrogen bonding with the ice surface [24]. This has been corroborated by the analysis of the energy distributions between the individual methanol molecules and ice phase, $P(U_b^{ice})$, and between the methanol molecules and other methanols in the system, $P(U_b^{meth})$, in GCMC simulations at 200 K [25] and also in MD simulations at 210 K [24]. Indeed, at full coverage of the ice surface, $P(U_b^{meth})$ exhibits a single peak at about -32 kJ/mol [25], a value that corresponds to the formation of one strong hydrogen bond between two neighbouring methanol molecules. Meanwhile, the $P(U_b^{ice})$ distribution shows that 50 % of the methanol molecules form one, whereas 50 % of them form two hydrogen bonds with the water molecules [25].

At lower coverage, the situation has been found to be different because of the larger distances between the adsorbed methanol molecules. In this situation, about 87 % of the methanol molecules are tied to the ice phase by two hydrogen bonds [25]. In addition, at low coverage, the mean value of the $P(U_b^{ice})$ distribution of -49.8 kJ/mol, is in a close agreement with the experimental value of the heat of adsorption (-51 ± 10 kJ/mol) measured at very low coverage [25]. A reasonable agreement between simulation and experimental results was also found for the adsorption isotherm as shown in Fig. 1c, especially at low p_{rel} values for which the Langmuir assumption is valid due to the weakness of the lateral interactions between the admolecules [24,25]. Finally, the maximum number of methanol molecules forming a monolayer on ice has been estimated to be about 5.8 ± 0.8 and 10 ± 0.5 $\mu\text{mol}/\text{m}^2$ in MD [24] and GCMC [23] simulations, respectively, in accordance with the estimation coming from the experimental measurements, $N_{max} = 7.0 \pm 1.0$ $\mu\text{mol}/\text{m}^2$ [25].

At the higher temperature of 250 K, MD simulations have shown that the upper layers of ice were much more disordered and the adsorbed molecules were found to be easily incorporated into the outermost layers that exhibit a liquid-like behaviour [24]. This penetration of the molecules inside the ice crystal has to be related to the difference in the solvation free-energy profile at the free surfaces of ice and liquid water, as simulated by Cavity Insertion Widom MC calculations [52]

Similar behaviour has been evidenced for formic acid [30,31] and acetone [34,35] molecules adsorbed on ice at relatively low pressures. Indeed, at the very beginning of the adsorption process (*i.e.*, at low pressure), when the adsorbed molecules are sufficiently isolated from each other, the Langmuir assumption appeared to remain valid, as shown by the isotherms given in Fig. 2a as a function of the relative pressure, and the simulated isotherms compared quite well with the corresponding experimental measurements [23,31,35]. At higher pressures, the adsorption of these molecules on ice is clearly of non-Langmuir nature (Fig. 2b), due to the presence of strong lateral interactions in the adlayer, related to the formation of hydrogen-bonds between the adsorbed molecules. These hydrogen bonds are in competition with the hydrogen-bonding to water regarding the stabilization of the adlayer [30,31,34,35]. It thus turned out that the adjustment of the Brunauer-Emmett-Teller (BET) isotherm to the simulated data points, although still not ideal, is much more adapted than the Langmuir one, up to a relative pressure of 0.35 [23]. Above this p_{rel} value, simulations clearly indicated evidences for the beginning of multilayer adsorption, and it clearly appeared that both formic acid and acetone molecules exhibited a quite complex behaviour at the ice surface, above the coverage corresponding to the failure of the Langmuir assumptions. Indeed, non equivalent adsorption sites have been evidenced for both molecules,

differing in the orientation of the admolecules and in the number of hydrogen bonds that they formed with the ice surface [31,35].

The calculated value of the adsorption energies at low coverage, *i.e.*, in the pressure region where the Langmuir assumption holds, was equal to -61.0 kJ/mol for formic acid in both MD [30] and GCMC [31] simulations, in close agreement with the experimental measurement of the heat of adsorption (-54 ± 8 kJ/mol) [31]. For acetone, these values were equal to about -43 kJ/mol in MD [34], -51 kJ/mol in GCMC, however, with a different potential model [34], and between -32 ± 6 and -54.4 ± 7.6 kJ/mol in the experiments, depending on the experimental method used.

The reasonable agreement between the simulated and measured adsorption isotherms, as well as the ability of MD and GCMC simulations to reproduce quite well the experimental heat of adsorption gives us confidence in the adequacy of the potential models used and, thus, in both approaches used and the results of the corresponding calculations.

We have also characterized the adsorption of formaldehyde on ice, a molecule for which, to the best of our knowledge, only scarce experimental results are available [70]. Again, both MD and GCMC simulations have been performed in similar conditions [22-24,27]. For this molecule, the adsorption isotherm is characterized by the lack of any plateau (Fig. 3a), indicating that no saturated adsorption layer is stable at the ice surface, contrarily to methanol and formic acid, as discussed above. As a consequence, the formaldehyde adsorption isotherm has been well fitted by the Langmuir isotherm up to the saturated vapour pressure p_0 (Fig. 3b), and this has been attributed to the weakness of the lateral interactions between the adsorbed molecules [24,27]. Similarly, the interaction between formaldehyde and ice is much weaker than what has been calculated for the three other molecules considered above, coming from

the fact that the formaldehyde molecules can form only one hydrogen-bond with the water molecules of the ice surface [23,24,27]. This weak interaction between formaldehyde and ice precludes any experimental measurements of the heat of adsorption [70], which has been calculated to be equal to about -30 kJ/mol at very low surface coverage both in MD [24] and GCMC [27] simulations. Finally, MD simulations at higher temperatures (250 K) showed both the solvation of the formaldehyde molecules in the uppermost liquid-like layers of ice and, interestingly, desorption from the ice surface, again in connection with the weak formaldehyde-ice interactions [24].

To summarize this first part of the present review, we showed that simulation results and experimental measurements are in quite good agreement for the four simple organic molecules considered. In addition, experimental information can be well complemented by the detailed analysis of the simulation results, at the molecular scale. Moreover, the behaviour of these molecules at the ice surface appeared clearly related to their chemical function, *i.e.*, to their ability to form hydrogen bonds not only with the water molecules of the surface but also with each other within the adsorption layer.

3.2. Adsorption of more complex organic molecules on crystalline ice.

The approaches developed for the four simplest organic molecules studied above have then been used to characterize the details of the adsorption process of more complex organic molecules at the crystalline ice surface.

MD simulations, performed at 193 and 223 K, in accordance with experimental conditions, have shown that the saturation coverage of ethanol at the surface of ice is equal to about $3.2 \pm 0.2 \times 10^{14}$ molecule cm^{-2} (*i.e.*, 5.3 ± 0.3 $\mu\text{mol m}^{-2}$) with an adsorption energy of -56.6 kJ/mol, in a good agreement with the corresponding

experimental values ($2.8 \pm 0.8 \times 10^{14}$ molecule cm^{-2} and $\Delta H_{ads} = -57 \pm 8$ kJ/mol) [26]. When adsorbed on ice, the ethanol molecule has been found to be in a tilted orientation, in such a way that the ethyl group points away from the surface, and the OH group is directed toward the water molecules with which hydrogen bonds are formed. Indeed, 55 % of the ethanol molecules were found to be involved in hydrogen bonding with water, acting as proton-donors, whereas 42 % of them as proton acceptors. Meanwhile, 43 % of the ethanol molecules have also been found to bind to their neighbours via lateral hydrogen bonds.

A similar combined experimental theoretical study has also been conducted to characterize the adsorption of acetic acid on ice between 193 and 223 K [32]. It has been shown that the interaction with the ice surface is able to split the acetic acid dimers that may exist in the gas phase into adsorbed monomers, leading to the formation of a molecular monolayer of acetic acid at the surface of ice, as shown by the distribution function of the acetic acid positions above the ice surface (Fig. 4a), with the saturation coverage of $3.7 \pm 0.2 \times 10^{14}$ molecule cm^{-2} (*i.e.*, 6.1 ± 0.3 $\mu\text{mol m}^{-2}$) and the adsorption energy of about -70.0 kJ/mol. At the ice surface, the acetic acid molecules are adsorbed with their carboxyl groups directed toward the water molecules (Fig. 4b) allowing the optimization of their hydrogen bonding with the ice surface and within the neighbouring adsorbate molecules (Fig. 4c). Both proton donor and proton acceptor configurations have been evidenced for the acetic acid molecules on ice through their hydroxylic and carboxylic groups [32].

Finally, MD simulations have also been used to study the adsorption of the bi-functional oxalic acid [33] and hydroxyacetone [36] molecules on ice at tropospheric temperatures, again in a close connection with the results of experimental investigations [33,71]. In these studies, the oxalic acid–water interaction has been found to be very

strong at infinitely small surface coverage due to the possible formation of a large number of hydrogen bonds between the adsorbed oxalic acid and the surface water molecules. By contrast, at monolayer coverage, MD simulations have shown the predominant role played by the oxalic acid–oxalic acid lateral interactions, which have been found to be even stronger than the water-water and water-oxalic acid interactions [33]. Interestingly, these strong lateral interactions have been found to play a crucial role in the desorption process observed when increasing the temperature. Indeed, MD results have shown the formation of oxalic acid aggregates at the ice surface at 240 K, preventing oxalic acid desorption [33]. Moreover, the holes formed within the oxalic acid layer due to the formation of these aggregates at 240 K, allows the departure of water molecules before the desorption of oxalic acid takes place, in accordance with experimental observations which suggested diffusion of water through the oxalic acid layer to explain the results of temperature programmed desorption experiments [71].

Concerning the adsorption of hydroxyacetone, the comparison between the results of MD simulations and those obtained from experiments using a coated wall flow tube between 213 and 253 K have shown that the calculations overestimated the energy of the adsorption by about 20 %, certainly due to some failure of the water/hydroxyacetone model used in the simulations [36]. In spite of this discrepancy, both the measured and the calculated adsorption enthalpies have found to be between – 63 and – 80 kJ/mol, *i.e.*, in a considerably lower energy range than what was obtained previously for other oxygenated volatile organic compounds. This finding has been related to the fact that each hydroxyacetone molecule can form, on average, three hydrogen bonds with the surface water molecules [36].

Having found the interaction between formaldehyde and ice to be very weak, we had the will to check whether this is true for other types of aldehydes. Thus, a longer

chain aldehyde molecule, namely acetaldehyde [28], and a cyclic one, *i.e.*, benzaldehyde [29] have been considered by coupling experimental investigations and GCMC simulations. As shown in Fig. 5a, the simulated isotherm for acetaldehyde on ice at 200 K exhibits a nice Langmuir shape in the entire pressure range of the existence of the vapor phase acetaldehyde (*i.e.*, up to $p_{rel} = 1$). This has been attributed to the monomolecular character of the adsorption layer up to the point of condensation and to the quite weak lateral interactions between the adsorbed molecules, similarly to what was seen for formaldehyde [27]. Acetaldehyde molecules have been found to be attached to the ice surface by one single acceptor hydrogen bond, with a strong preference for an orientation in which the plane of the molecule is aligned perpendicularly to the ice surface, irrespective of the acetaldehyde coverage. In this configuration, the methyl group of the molecule is located as far as possible from the water molecules, in accordance with experimental conclusions drawn from infrared spectroscopy measurements [28]. At infinitely low surface coverage, the heat of adsorption has been estimated to be -36 ± 2 kJ/mol in the experiments, very close to the calculated value of -34.1 kJ/mol. This value is about 20 % lower than what was previously obtained for formaldehyde [27].

The situation has turned out to be somewhat different for benzaldehyde since the calculated adsorption isotherm clearly departed from the Langmuir behavior above $p_{rel} = 0.3$, due to the stronger influence of the intra-adsorbate interactions at moderate and high surface coverages (Fig. 5b). Nevertheless, at lower pressures, *i.e.*, in the Langmuir regime, the simulated and experimental isotherms obtained at 233 K have been in excellent agreement with each other, as did the calculated (-59.4 ± 5.1 kJ/mol) and measured (-61.4 ± 9.7 kJ/mol) values of the heat of adsorption, confirming thus the validity of the computer model used [29]. At low surface coverage, the benzaldehyde

molecules have been found to be oriented parallel to the ice surface, in a configuration stabilized both by the formation of one hydrogen bond with a surface water molecule and by a strong interaction between the delocalized π electron system of the benzaldehyde molecule and an O atom of the ice surface. When the coverage has been increased, a more complex situation has been evidenced in the simulations. Namely, perpendicular orientation of the benzaldehyde molecules to the surface have also appeared to be favoured, leading to the presence of traces of a second molecular layer in the stable saturation adsorption layer and to the quite intricate shape of the benzaldehyde adsorption isotherm (Fig.5b)

Such an intricate shape has also been observed for the adsorption isotherm of H_2O_2 [46], one of the key players in the atmospheric oxidizing cycles. In accordance with experimental data of Pouvesle et al. [72], GCMC results have indicated a strong affinity of H_2O_2 to the ice surface, driven by the formation of new H-bonds between H_2O_2 molecules rather than between H_2O_2 and the surface water molecules. This has resulted in the formation of a rather thick layer of H_2O_2 at the surface of ice in the simulations, suggesting that a large part of the atmospheric H_2O_2 may be adsorbed at the surface of the ice grains.

3.3. Adsorption of small aromatic hydrocarbon molecules on crystalline ice.

Because aromatic hydrocarbon (AH) molecules are ubiquitous atmospheric pollutants that are known to be quite easily trapped by snow and incorporated into the snowpack [73-76], a thorough characterization of their interaction with ice surfaces at the molecular scale appeared to be very useful to better quantify the fate of these molecules both in the troposphere and in the boundary layer. We have thus performed GCMC and MD simulations [37,38] to study the adsorption of benzene, naphthalene, anthracene

and phenanthrene at the surface of ice I_h at the tropospheric temperature of 200 K [37] and in the temperature range of [250 – 270] K, more typical of the Arctic and subarctic snowpacks [38].

GCMC simulations at 200 K showed that the mechanisms of AH adsorption on ice is more complicated than what might be expected for apolar adsorbates and, again, demonstrated the delicate interplay of the ice–adsorbate and adsorbate-adsorbate interactions in determining the thermodynamic driving force of the adsorption [37]. Thus, up to a certain low relative pressure value (typically between 0.1 and 0.3 depending on the AH molecule considered), the adsorption is perfectly Langmuir-like. In the corresponding pressure range, the AH molecules have been found to be adsorbed parallel to the ice surface (Fig. 6), in such a way that the dangling OH bonds of the ice surface can form an O–H $\cdots\pi$ -type hydrogen bond with the delocalized π electrons of the aromatic molecule. In this low coverage region of the isotherm, i.e., when the lateral interactions between the admolecules are vanishingly small, adsorption energies have been calculated to decrease when the size of the adsorbed molecules increases, ranging from about – 40 kJ/mol (for benzene) to about – 95 kJ/mol, for phenanthrene [37].

At higher pressures, the newly arriving aromatic molecules interact much more strongly with the previously adsorbed molecules than with the ice surface, increasing thus the importance of the lateral interactions [37]. This leads to the increasing deviation of the adsorption isotherm from the Langmuir shape. However, for the four AH molecules considered, the adsorption layer has been found to remain strictly monomolecular up to the point of condensation, and it has been shown that condensation precedes even the saturation of this monomolecular layer in every case [37].

At higher temperatures, between 250 and 270 K, MD simulations performed on the phenanthrene/ice system have shown that the phenanthrene molecules stay adsorbed at top of ice, lying parallel to the ice surface with an adsorption enthalpy of -85 ± 8 kJ/mol at 260 K, in close agreement with experimental data (-89 ± 18 kJ/mol) [38]. This information, combined with the experimental conclusions, has been used to calculate the partitioning of phenanthrene between the snowpack and the atmospheric boundary layer, showing thus that, whereas the subarctic snowpack is a negligible reservoir of phenanthrene, the colder Arctic snowpack is certainly able to sequester most of the phenanthrene molecules present in the (snow + boundary layer) system [38].

3.4. Adsorption of halogenated methane derivatives on crystalline ice.

Halogenated hydrocarbon molecules play several important roles in a number of environmental issues, such as the formation of the Antarctic ozone hole [77], or global warming due to the greenhouse effect [78]. Halogenated hydrocarbons are long-living species in the atmosphere due to their low reactivity, particularly under tropospheric conditions. Adsorption at the surface of ice grains could thus participate in their atmospheric fate, and they can be scavenged from the troposphere by falling snow. Moreover, in the snow-covered part of the Earth (such as the polar regions), halogenated hydrocarbons might undergo specific oxidative and photochemical reactions, thus impacting the chemistry of the overlaying atmosphere (*i.e.*, the so-called “boundary layer”) [79,16].

To achieve a better understanding of the interaction between halogenated compounds and ice surface, we have recently performed a set of GCMC simulations investigating the adsorption of all the fluorinated and chlorinated methane derivatives ($\text{CH}_n\text{X}_{4-n}$, n ranging from 0 to 4, $\text{X}=\text{Cl}, \text{F}$) at the (0001) surface of I_h ice [40-42]. These

studies well complement well the partial results obtained from previous MD simulations on some of these molecules interacting with ice surface [39,80,81]. Because the results of our GCMC studies have been reviewed in a recent publication [43], only the main conclusions are recalled here.

We have found that the behaviour of the adsorption isotherms of halogenated methane derivatives on ice is determined by the interplay of the $\text{CH}_n\text{X}_{4-n}$ -ice and $\text{CH}_n\text{X}_{4-n}$ - $\text{CH}_n\text{X}_{4-n}$ interactions, i.e., of the adhesion and cohesion. Thus, for CH_3F and CH_2F_2 , because adhesion is considerably stronger than cohesion, multilayer adsorption has been observed in the simulations. For CHF_3 and CH_3Cl , these two interactions have been found to be of roughly equal strengths, leading to the formation of an adsorption monolayer. Moreover, in the case of CHF_3 , traces of multilayer adsorption has also been observed right before the point of condensation, and this has been related to the strength of adhesion that slightly exceeds that of cohesion. For the other adsorbates, cohesive interaction has been found to be much stronger than adhesion, and, consequently, no considerable adsorption has been seen, because the condensation of these adsorbates well precedes the formation of an adsorption layer of even moderate surface coverage. Note however that, in the case of the partially fluorinated methane derivatives, for which the cohesion has not been found to be too strong, the adsorption isotherms show a Langmuir character, at least up to the pressure above which multilayer adsorption occurs.

Molecular simulations have also revealed that the strength of the adhesion depends primarily on the possible H-bond formation between the adsorbate and the surface water molecules [39]. In addition, the stronger adsorption of the CH_3X relative to that of the CH_2X_2 and CHX_3 type molecules has clearly indicated that, from the point of view of the adsorption, the formation of more, though weaker H-bonds is

advantageous over that of one strong H-bond [43]. Finally, our results have also shown that the orientation of the $\text{CH}_n\text{X}_{4-n}$ molecules at the ice surface is such that at least one of their halogen atoms is exposed to the vapor phase [43], making it accessible for reactions with gas phase species, and also releasable in photodissociation processes, which could be of importance for further atmospheric impact.

3.5 Adsorption of methylamine on crystalline and amorphous ice.

Small amine molecules are common atmospheric and interstellar species that have attracted increasing attention due to their potential role in, *e.g.*, enhancing aerosol nucleation rates in the lower troposphere [82] and, also, as precursors of amino acids in the interstellar medium [83]. The common feature of the underlying processes is the interaction of these molecules with water or icy surfaces, and there is a strong need for a better characterization of the fate of amine molecules at the ice interface.

We have thus recently performed GCMC simulations to study the adsorption of methylamine (CH_3NH_2) at the surface of crystalline [44] and low density amorphous (LDA) [45] ice, in temperature ranges corresponding to either the upper troposphere or the cold interstellar regions.

On I_h ice, the simulated adsorption isotherm of methylamine at 200 K exhibited a plateau corresponding to the formation of a saturated stable monolayer in a remarkably broad range of pressures (Fig. 7a). This has resulted from a delicate competition between hydrogen bonding with surface waters and strong dipolar attraction between the neighbouring methylamine molecules, which is reflected by the non-Langmuir behaviour of the adsorption isotherm [44]. On I_h ice, the adsorbed methylamine molecules exhibit rather rich orientational preferences that are mainly governed by the requirement of maximizing the number of hydrogen bonds formed with

the surface water molecules at low surface coverage, and by antiparallel or head-to-tail near-neighbour orientations at higher coverage, in order to favor dipolar interactions between these neighbours [44].

Under similar conditions, GCMC simulations have shown that LDA ice has a higher adsorption capacity than I_h ice (as evidenced by the comparison of the adsorption isotherms given in Fig. 7a), primarily due to the larger surface area of the amorphous phase [45]. The ability of methylamine for being adsorbed at the surface of LDA ice has been shown to be also stronger than at the surface of ice I_h , a feature which is well reflected in the calculated heat of adsorption values at infinitely low surface coverage of -51.3 ± 3 kJ/mol on I_h ice and -69 ± 5 kJ/mol on amorphous ice (Fig. 7b). On LDA ice, it has also been found that adsorption of methylamine is strongly enhanced by the decrease of the temperature and even multilayer adsorption has been obtained in the simulations at high enough relative pressures [45]. The enhanced adsorption capacity of amorphous ice has been related to the formation of up to three hydrogen bonds between methylamine and the surface water molecules which, at the surface of amorphous ice, contrarily to that of crystalline ice, do not exhibit any orientational preference. In addition, the GCMC results have shown that a non negligible amount of methylamine molecules are dissolved in the bulk LDA phase [45].

To summarize, our GCMC calculations have shown that methylamine strongly interacts with the surface of both crystalline and amorphous ice at the low temperatures typical of the upper troposphere and of the interstellar medium [44,45]. Thus, significant fractions of methylamine molecules may be scavenged from the gas phase by trapping at the surface of ice particles in cirrus clouds. Similarly, the trapping of large amount of methylamine by solid water at the surface of interstellar grains or in

comets can be well expected, giving rise to subsequent chemical/photochemical reactions that may participate in prebiotic chemistry.

4. Conclusion

In this paper, we reviewed 15 years of simulation studies devoted to the detailed characterization, at the molecular scale, of the adsorption of various organic compounds, being representative of atmospheric trace gases, on ice [22-43]. We also briefly illustrated the difference between the adsorption on crystalline and amorphous ice surfaces by using methylamine as an example, since it is an adsorbate of both tropospheric and interstellar interest [44,45].

When possible, the comparison between the results of the simulations and available experimental data has shown a sufficiently good agreement, giving confidence both in the methodology used in the simulations and in the interaction potential models considered in the calculations [26,28,29,31,32,36,38].

In every case, it has been shown that the main thermodynamic driving force of the adsorption at low pressure is the possibility of the formation of hydrogen bonds between the adsorbate and the surface water molecules. At higher pressures, corresponding to larger surface coverage, a strong competition between the adsorbate-surface and the adsorbate-adsorbate interactions has been evidenced, which may even lead to the condensation of the adsorbate before the completion of a full monolayer at the ice surface. With the exception of the formaldehyde [27] and the acetaldehyde [28] molecules, for which an almost perfect Langmuir behaviour has been evidenced up to the condensation pressure, the simulated adsorption isotherms exhibit a Langmuir behaviour up to a threshold pressure only, above which the lateral interactions starts to become non-negligible. This deviation from the Langmuir behaviour should certainly be

taken into account when estimating the monolayer capacity of the adsorbate (i.e., the maximum number of molecules that can form a monolayer at the ice surface), which is used to calculate the fraction of molecules scavenged by, *e.g.*, ice particles of cirrus clouds [17,29,36]. Indeed, scavenging of organic molecules from the atmosphere by trapping at the surface of ice has been shown to be quite weak in most cases [10], but might be underestimated due to the Langmuir hypothesis. Note also that, even within the Langmuir approximation, sufficiently strong interactions between some adsorbed species and ice, as calculated, *e.g.*, for hydroxyacetone, may lead to an efficient scavenging from the gas phase, at least at the lowest temperatures of the troposphere [36]. Similarly, very large adsorbing surface areas of ice, as in the polar regions, can also lead to non-negligible trapping of atmospheric pollutants [10,38].

These conclusions, as well as the details, at the molecular scale, of the results obtained from 15 years of simulations, emphasize the fact that each trace gas has a specific behaviour at the surface of ice, which can hardly be predicted. Indeed, the interaction with ice strongly depends on the chemical type of the molecule and can be complicated by the presence of different chemical groups in the admolecule, in addition to the usual separation between hydrophilic head and hydrophobic tail. An instructive illustration of this feature is the benzaldehyde molecule. Indeed, its interaction with ice could be assumed to be weak simply because it is an aldehyde-type molecule. However, because surface waters can form a quite strong H-bond with the delocalized π electrons, this adsorbed molecule behaves rather as an aromatic adsorbate on ice [29].

These conclusions emphasize the urgent need for systematic studies, in particular, for large, complex molecules in order to answer the important questions concerning the fate of numerous chemicals in the atmosphere and the role that ice surfaces can play in the corresponding processes [14]. In this respect, simulations can

nicely complement more expensive experimental investigations and even explore thermodynamic conditions that are not easily accessible by experiments. This is a strong motivation for further works and, indeed, several recent papers already use approaches very similar to those presented here [84-86].

It is also worth mentioning that state-of-the-art *ab initio* calculations can nicely help at characterizing the details of the adsorption mechanisms on ice, especially when chemical reactions likely occurs [87-89]. Although the corresponding studies are often limited to a quite small number of adsorbed molecules, their results, based on quantum chemistry calculations, can support the accuracy of simulation studies based on empirical interaction potentials and, thus reinforce the corresponding conclusions, at least for the first steps of the trapping, i.e., before possible (photo)chemical processes take place.

Finally, it has not be noted that molecular-scale simulations have also turned recently to much more complex systems, such as organic aerosols, in order to understand how they can act as condensation nuclei for atmospheric ice particles [90-102]. These simulations, as those reviewed here, involve a thorough modeling of the interactions between various, complex organic compounds and water molecules in tropospheric conditions.

To conclude, as already stated in most of our publications, adsorption of organic molecules on ice represent an interesting topic for which simulation and experimental approaches can nicely complement each other. Indeed, we have shown that the simulation results can provide a deeper insight into the molecular-level details of the adsorption process than any experiment can do, whereas the relevance of the theoretical results can only be verified and improved by comparison with existing experimental data.

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Figure captions

Figure 1 : (a) Average number of methanol molecules in the basic simulation box as a function of the methanol chemical potential as calculated from GCMC simulations performed on the methanol/ I_h ice system at 200 K [25]. Some snapshots issued from the simulations are also given to illustrate the geometry of the methanol layer(s) at various chemical potential values; (b) Adsorption isotherm (black circles) for methanol on ice at 200 K in the $\Gamma(p_{rel})$ form together with the corresponding Langmuir fit (black curve) [23]; (c) Comparison between the simulated (asterisks) adsorption isotherm of methanol on ice, and the experimentally measured isotherms at 198 K (circles) and 200 K (squares) [25] (note that the lines connecting the simulated data points are just guide to the eye).

Figure 2 : (a) Simulated adsorption isotherms (black circles) and the corresponding Langmuir fit (solid curves) at low relative pressure and (b) simulated adsorption isotherms (black circles) in the entire pressure range for formic acid and acetone molecules adsorbed at the surface of ice at 200 K, as issued from GCMC calculations [23,31,35].

Figure 3 : (a) Simulated adsorption isotherms of formaldehyde on ice (black circles) in the $\langle N \rangle(\mu)$ form, as obtained from GCMC simulations at 200 K (a snapshot issued from the simulation is also given to illustrate the geometry of the adlayer) and (b) Langmuir isotherm fitted to the simulated data (solid lines) in the entire relative pressure range [23,27].

Figure 4 : Some results obtained from the MD simulations of 60 acetic acid molecules adsorbed on I_h ice at 193 K [32]: (a) Distribution function (in arbitrary units) of the distance z (in Å) of the water (black curve) and acetic acid (blue dots) centers of mass,

from the bottom of the MD box (note that only the top layers of the ice system are considered in this figure); (b) side and (c) top views of one snapshot issued from the simulation. Red, gray, and white circles represent O, C, and H atoms, respectively. For clarity, the water molecules are represented as small sticks in the side view, whereas they are not represented in the top view. Formation of acetic acid dimers are also indicated in the top view (dark ovals)

Figure 5 : Simulated adsorption isotherms of (a) acetaldehyde [28] and (b) benzaldehyde [29] on ice (black circles) in the $\Gamma(p_{rel})$ form, as obtained from GCMC simulations at 200 K (some snapshots issued from the simulation are also given to illustrate the geometry of the adsorbate at various pressure values). The solid line represents the Langmuir isotherm fitted to the simulated data.

Figure 6 : Instantaneous equilibrium snapshots coming from GCMC simulations of the (a) benzene, (b) naphthalene, (c) anthracene, and (d) phenanthrene molecules adsorbed on ice surface at 200 K, at the chemical potential value that just precedes condensation [37]. Water and adsorbate molecules are represented by blue and red sticks, respectively

Figure 7 : (a) Simulated adsorption isotherms of methylamine on crystalline I_h ice (empty circles [44]) and on amorphous ice (black circles [45]) in the $\Gamma(p_{rel})$ form, as obtained from GCMC simulations at 200 K. (b) Distribution of the total binding energy U_b of the first layer methylamine molecules, as obtained at 200 K at the surface of crystalline (I_h) ice (open symbols), and at that of amorphous ice (full symbols) at the chemical potential values of -35.5 kJ/mol (red), -42.2 kJ/mol (blue), and -47.2 kJ/mol (orange) [45].

Figure 1.

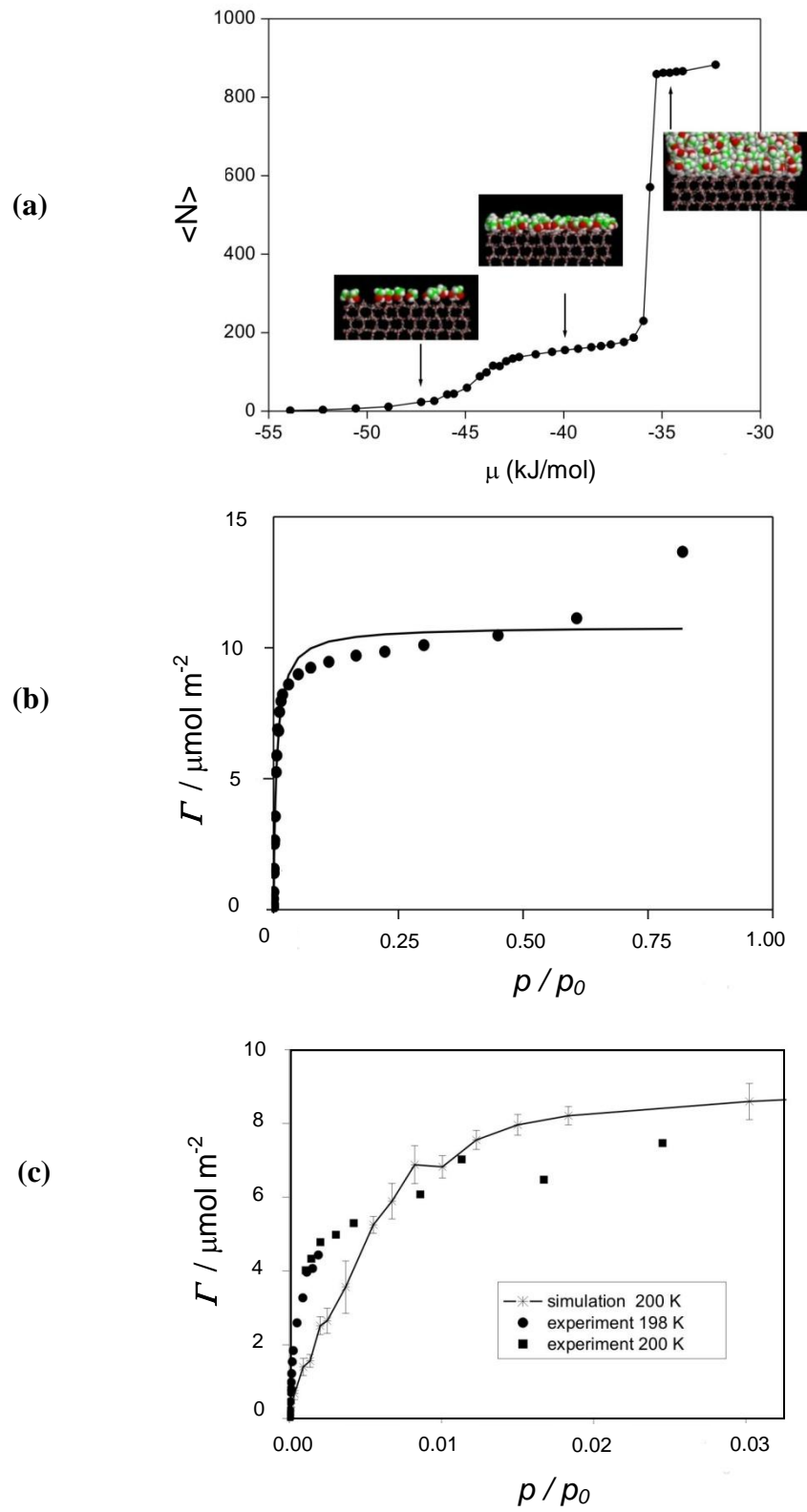


Figure 2.

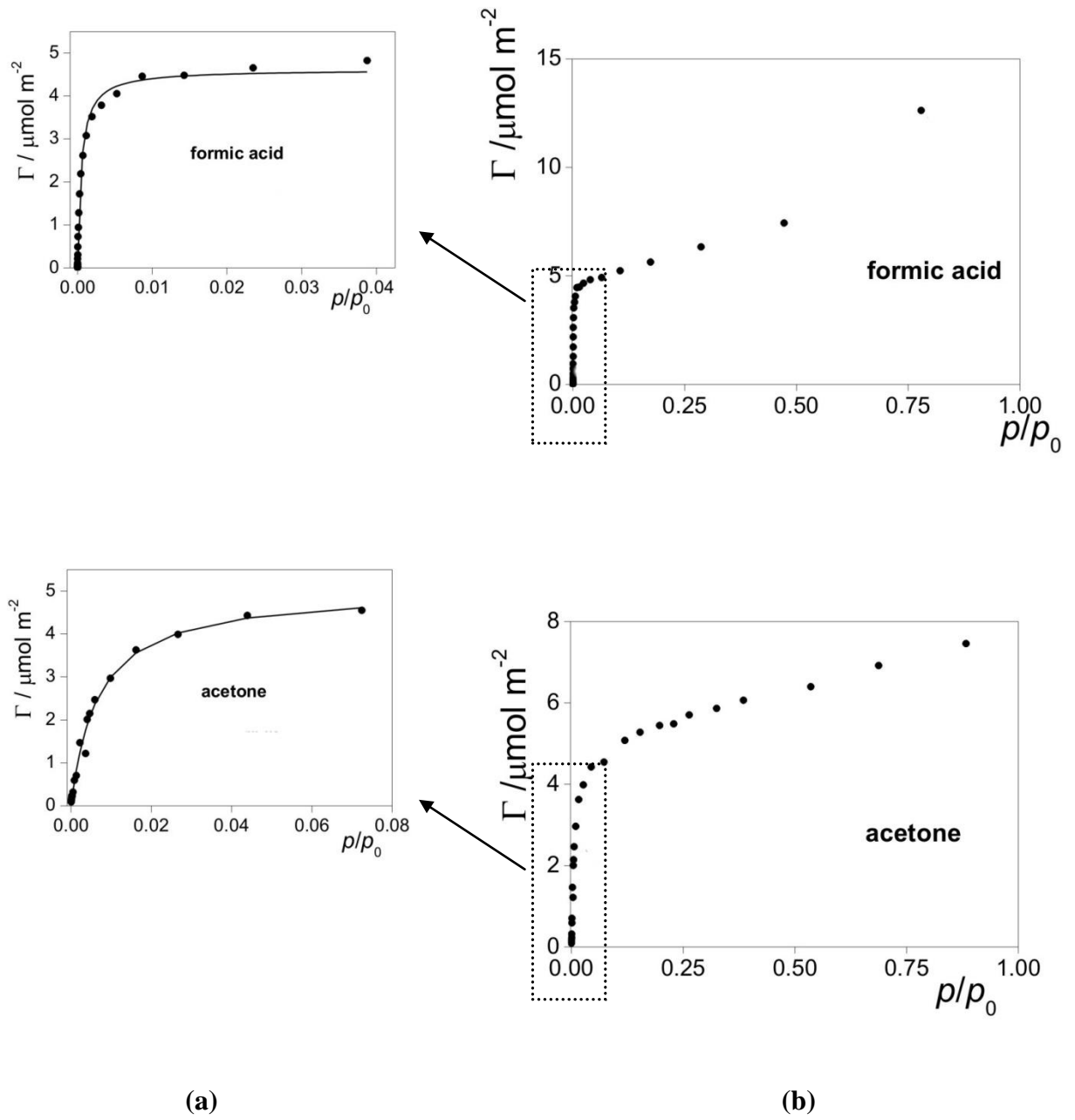


Figure 3.

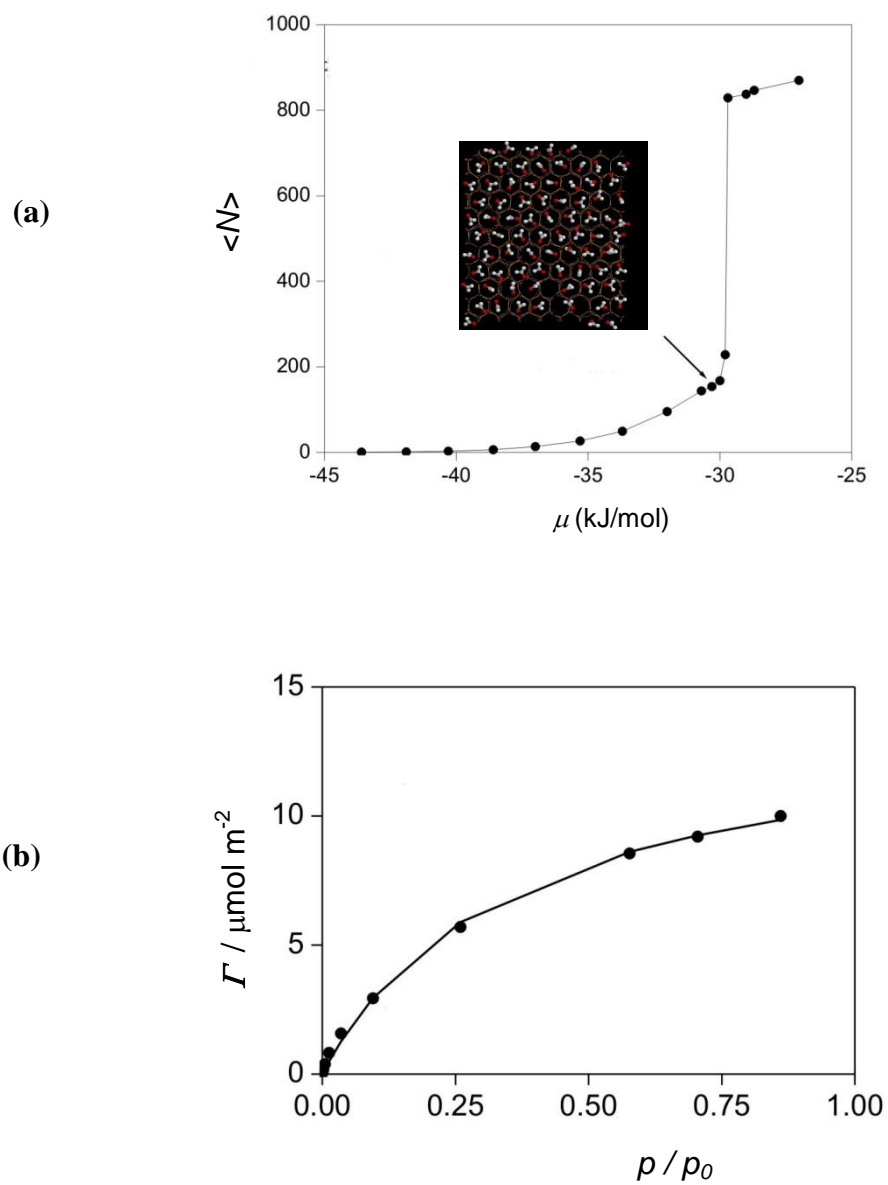


Figure 4.

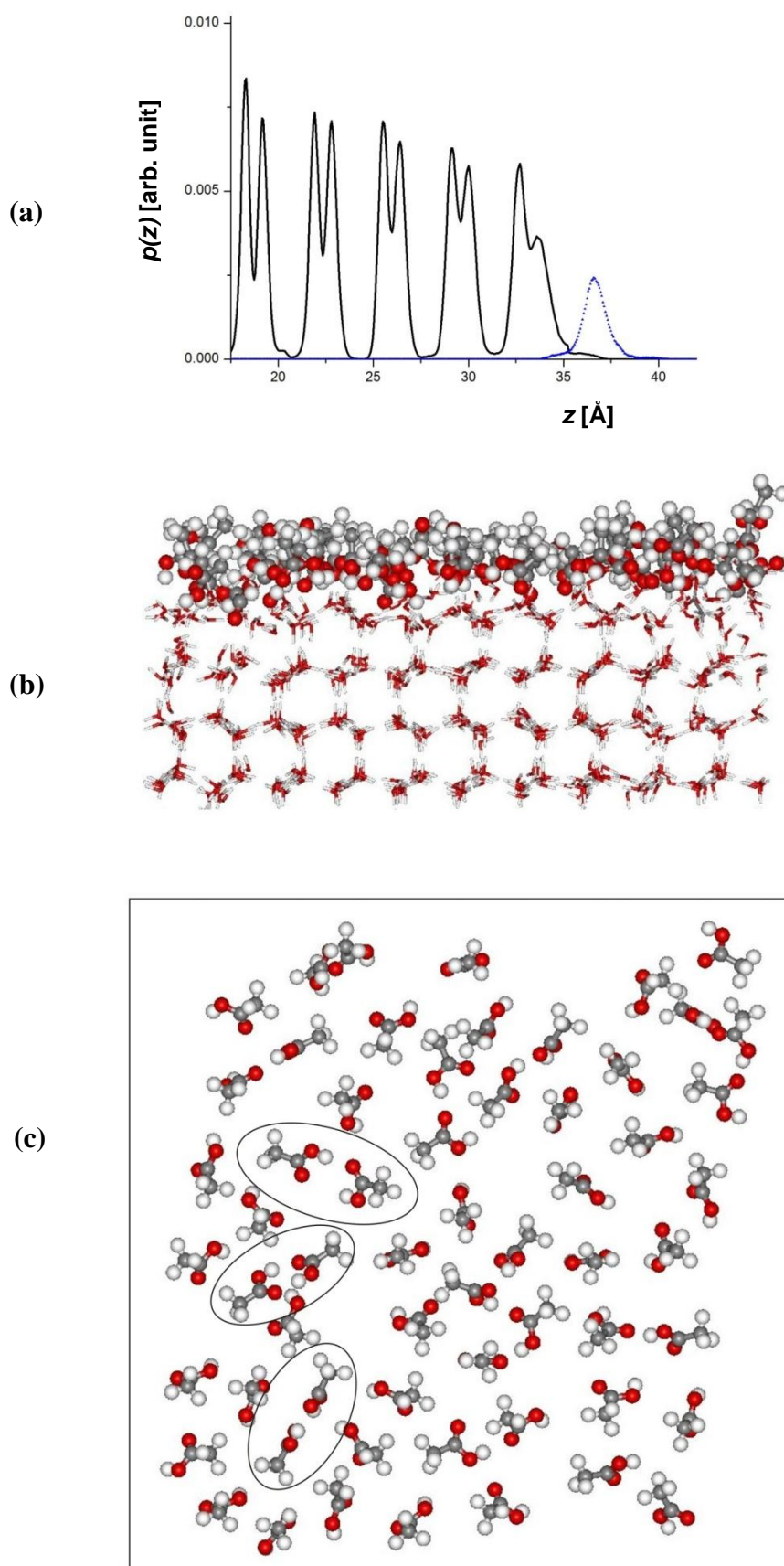


Figure 5.

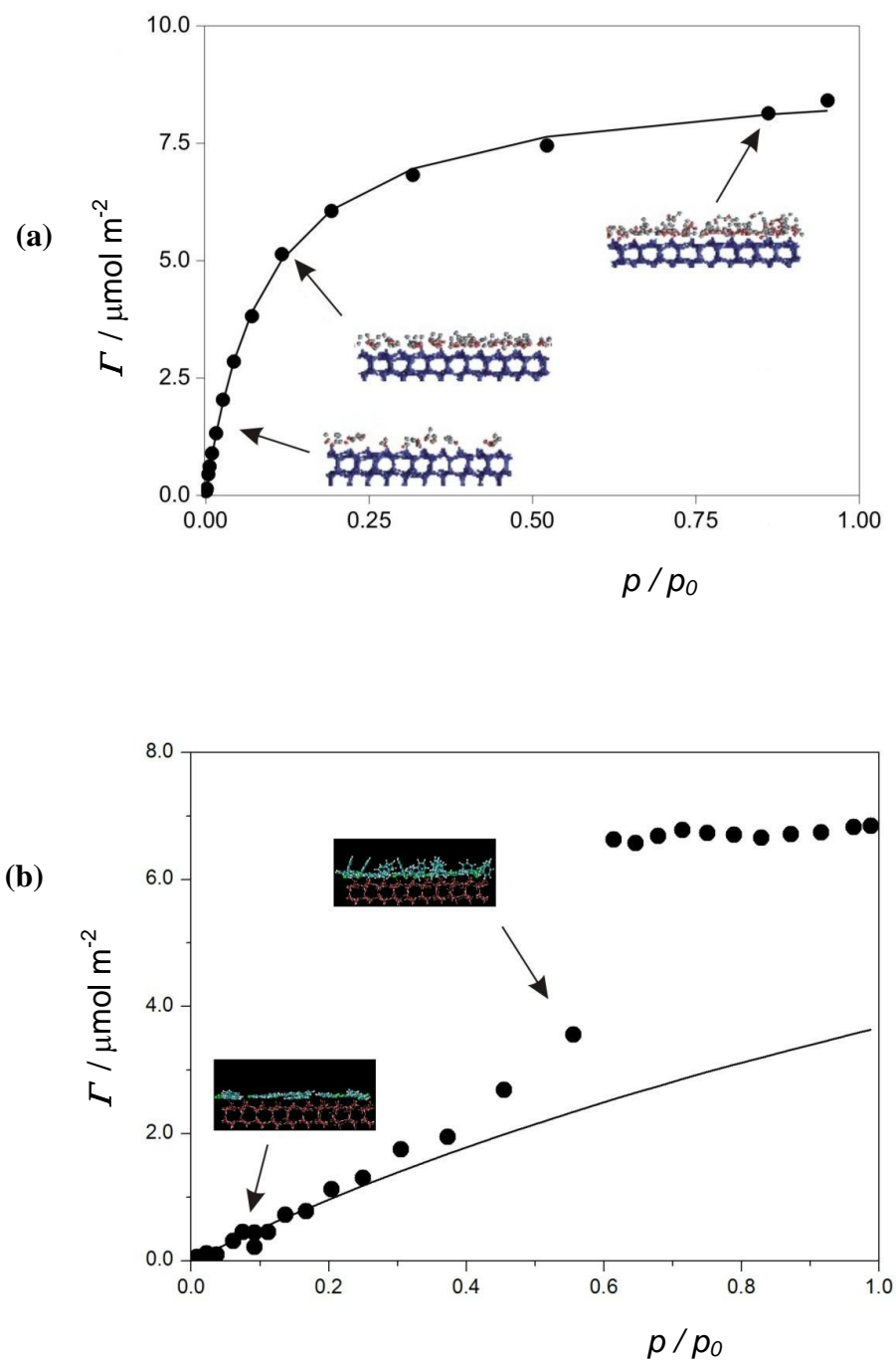
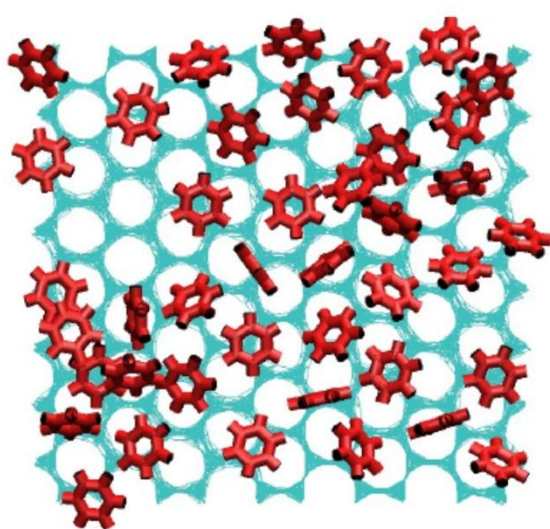
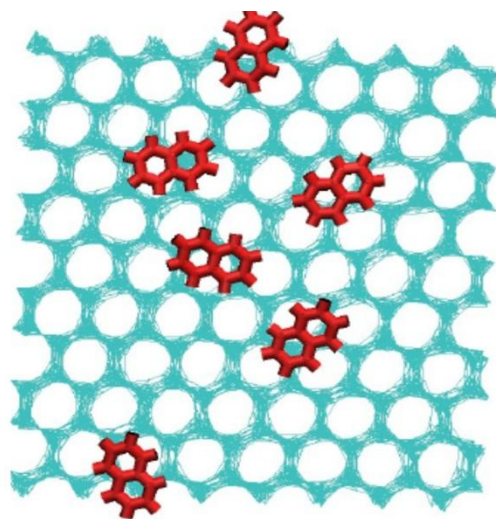


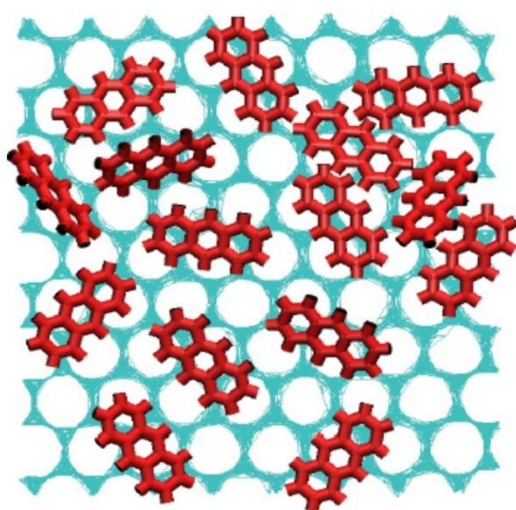
Figure 6.



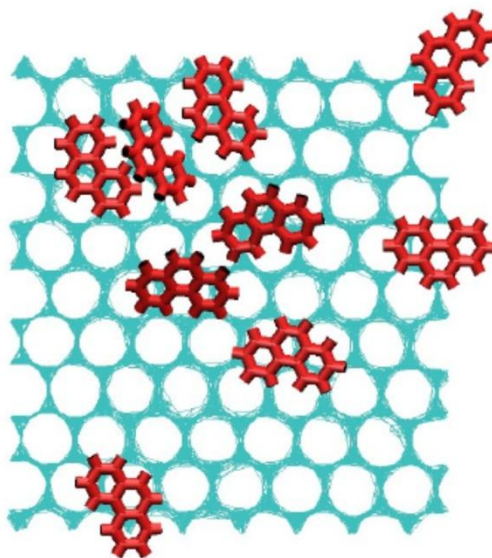
(a)



(b)



(c)



(d)

Figure 7.

