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Julien Joliat, Sylvain Picaud, Pál Jedlovsky. Competitive Adsorption of Trace Gases on Ice at Tropospheric Temperatures: A Grand Canonical Monte Carlo Simulation Study. *Journal of Physical Chemistry A*, 2023, 127, pp.10223-10232. 10.1021/acs.jpca.3c04789 . hal-04311371v2

HAL Id: hal-04311371

<https://hal.science/hal-04311371v2>

Submitted on 10 Apr 2024

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Competitive Adsorption of Trace Gases on Ice at Tropospheric Temperatures : A Grand Canonical Monte Carlo Simulation Study.

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Abstract

The co-adsorption of two atmospheric trace gases on ice is characterized by using, for the first time, Grand Canonical Monte Carlo (GCMC) simulations performed in conditions similar to those of the corresponding experiments. Adsorption isotherms are simulated at tropospheric temperatures by considering two different gas mixtures of 1-butanol and acetic acid molecules, and selectivity of the ice surface with respect to these species is interpreted at the molecular scale, as resulting from a competition process between these molecules for being adsorbed at the ice surface. It is thus shown that the trapping of acetic acid molecules on ice is always favored with respect to that of 1-butanol at low pressures, corresponding to low coverage of the surface, whereas the adsorption of the acid species is significantly modified by the presence of the alcohol molecules in the saturated portion of the adsorption isotherm, in accordance with the experimental observations. The present GCMC simulations thus confirm that competitive adsorption effects have to be taken into consideration in the real situations, when gas mixtures present in the troposphere interact with the surface of ice particles.

Introduction

Gas/ice interfaces are ubiquitous in atmospheric environments, where they influence the local chemistry by acting as trace gas scavengers or as catalysts for heterogeneous surface reactions that may strongly differ from gas phase processes.¹⁻⁴ Thus, many laboratory studies have been devoted to the characterization of the trapping properties of various atmospherically relevant molecules, ranging from weakly (e.g., small organic compounds, such as formaldehyde) to very strongly (e.g., inorganic acids, such as HNO_3) interacting species on ice, at tropospheric temperatures.^{2,3} Meanwhile, some of these experimental data have nicely been complemented by results coming from numerical simulations, based on the description of the gas/ice interactions at the molecular scale.⁵ In these framework, Monte Carlo simulations performed in the grand canonical ensemble (GCMC)⁶ have proven to be one of the most suitable modeling approaches,^{5,7} because GCMC directly provides the adsorption isotherm, being one of the observables most commonly recorded in the experiments. Thus, maximum surface coverage as well as adsorption energy can be provided on both experimental and theoretical sides for comparison, which allows, for instance, assessment of the interaction potential models used in the simulations.

Laboratory studies of atmospherically relevant adsorption processes have most often been conducted with a single species, and so has also been done by the modeling approaches. However, taking into account the large variety of organic species emitted in the atmosphere, it is also of fundamental importance to characterize how the competition for occupying similar adsorption sites may change the trapping efficiency of the ice surface when different species are simultaneously present.⁸ Despite the expected importance of such co-adsorption processes, it is disappointing to note that, as far as we know, only two, relatively old such laboratory studies have been published so far.^{8,9} This could, nevertheless, be explained by the corresponding experimental constraints. However, the situation is even worse from the theoretical side, as no study has provided a detailed, molecular-level understanding of the simultaneous adsorption of several compounds on ice.

Again, the GCMC method is an ideal tool to tackle such a challenge, as it has proven to give a realistic description of the selective trapping of small volatile species in multi-guest clathrate hydrates, in various contexts relevant for astrophysical situations.^{10–13} Thus, based on the experience we have acquired by using the GCMC method to characterize, on one hand, the adsorption of one single organic species on ice⁵ and, on the other hand, the competition between different species to occupy the cages of clathrate hydrates,^{10–13} here we present the results of the first molecular scale simulation study of a competitive adsorption process on ice under tropospheric conditions.

As a first application, we have chosen to investigate the case of mixtures of 1-butanol and acetic acid molecules, i.e., two small, polar, oxygenated organics that are abundant in the atmosphere.^{14–16} The choice of these adsorbates is also dictated by the fact that their co-adsorption on ice has previously been investigated in coated-wall flow tube experiments,⁸ opening thus the possibility of comparing the present results to the experimental data.

Computational Details

Water molecules have been described by the TIP4P/Ice model,^{17,18} whereas the 1-butanol and the acetic acid molecules have been modeled with the flexible AUA4 potential.^{19,20} Note that previous simulation studies have shown the relevance of this combination of interaction potential models to accurately describe the behavior of the 1-butanol molecules on ice.²¹ Both the TIP4P/Ice and the AUA4 models are defined as sums of pairwise dispersion-repulsion and electrostatic terms, represented by Lennard-Jones (LJ) and Coulomb interactions. Heteronuclear interactions have been calculated in the same way, using the cross LJ parameters determined according to the standard Lorentz-Berthelot combination rules.²² Analytical tail correction⁶ has been applied for the LJ contributions to the interaction potential, while the long-range part of the electrostatic interaction has been accounted for by means of the Ewald summation method.²²

Ice grains have been simulated by a slab made of 2880 water molecules, arranged in 18 solid layers stacked along the 0001 crystallographic axis (defining the z axis of the system). This ice slab has been placed in a rectangular simulation box of the dimensions of $L_x = 35.926 \text{ \AA}$, $L_y = 38.891 \text{ \AA}$, and $L_z = 100 \text{ \AA}$, in such a way that the slab exhibits two interfaces in contact with the gas phase, consisting of the 1-butanol and acetic acid molecules, along the z axis. Periodic boundary conditions have been applied along all the three axes and a cut-off radius equal to half the smallest size of the simulation box has been applied for the calculation of the interactions. Thus, two molecules pertaining to the two opposite interfaces have not interacted with each other directly. The simulations have been performed using the GIBBS software, which is a general Monte Carlo simulation code, developed jointly by three French Institutions (Université Paris Sud, CNRS and IFPEN),²³ and which has been used here under a Licence freely provided.

To characterize the adsorption properties of a gas phase containing a mixture of 1-butanol and acetic acid molecules, GCMC runs have been performed, allowing the number of the adsorbate molecules to fluctuate in the simulation box with the value of the total chemical potential μ . For each μ value considered, the number of molecules of each species that are in contact with the ice surface has been determined. This number of adsorbed molecules as a function of μ corresponds, by definition, to the adsorption isotherm for a given composition of the gas phase and a given temperature. For comparisons with experimental data, the results of such simulations have, however, been expressed in terms of pressure instead of chemical potential, using a conversion procedure consistent with the interaction potential models, for the selected compositions of the gas phase, as in our previous works^{13,21,24} (see also the Supporting Information).

The GCMC simulations have started with a period of equilibration of typically $2 - 4 \times 10^8$ Monte Carlo steps. Once the energy of the system and the number of molecules in the basic box started to fluctuate around their equilibrium values, a production run of 2×10^8 Monte Carlo steps has been performed. The 1-butanol and acetic acid molecules have been flexible,

while the water molecules have been kept rigid, in accordance with the parametrization of the TIP4P/ice model.^{17,18} Thus, in the simulations, the water molecules have only been subject to translational and rotational moves, performed with equal probabilities, while for the 1-butanol and acetic acid molecules, insertion (20 %), deletion (20 %), translation (15 %), rotation (15 %), configurational-biased regrowth (i.e., change of the internal molecular configuration, 15%) and identity swap (i.e., one molecule of a given type is replaced by a molecule of the other type, at the same position, 15%) moves have been attempted.

Results and Discussion

Our previous works showed that the simulated adsorption isotherms of small alcohols on ice compare very well with experimental data, provided that a small (i.e., about 5 K) temperature shift is considered in the calculations.^{7,21} For this reason, the present simulations have not only been performed at the temperature of the experiments of 228 K, but also at 233 K. However, only the results obtained at this slightly higher temperature are detailed here, because they indeed show an overall better agreement with the experimental data, in particular, when looking at the low pressure part of the adsorption isotherms, as discussed below. Note that we have not studied the adsorption process at higher temperatures, the main goal being, in this first simulation study of the competitive adsorption process, to stay as close to the experimental conditions as possible, for the purposes of validating our GCMC approach.

Adsorption isotherms

The simulated adsorption isotherms at 233 K are shown in Figure 1 for four various compositions of the gas mixture, corresponding to the gas phase 1-butanol:acetic acid molar ratios of 100:0, 62:38, 25:75, and 0:100. These compositions have been chosen in accordance with the experimental conditions, considering both species separately, and also two mixtures, charac-

terized by gas partial pressure ratio of $P_{1\text{-butanol}} = (1.65 \pm 0.15) \times P_{\text{acetic acid}}$ (corresponding to the molar ratio of 62:38) and $P_{\text{acetic acid}} = 3.1 \times P_{1\text{-butanol}}$ (i.e., molar ratio of 25:75).⁸ Note that the experimental data at 228 K,⁸ extracted from the original publication using the WebPlotDigitizer software,²⁵ are also reported on Figure 1, for comparisons.

At first, we discuss the adsorption of 1-butanol and acetic acid in the respective neat systems. As seen from Figure 1 (top row), the adsorption behavior of the two molecules is rather similar to each other in the low pressure range, where a rapid increase of their surface concentration, Γ , corresponding to the building up of the adsorption layer at the surface, is observed. It should, however, be noted that the adsorption process starts at much lower pressures for acetic acid than for 1-butanol and, as a consequence, in the low pressure range, up to about 5×10^{-3} Pa, the amount of acetic acid molecules trapped at the ice surface is considerably larger than that of the alcohol molecules. The increase of the pressure above 2×10^{-2} Pa only leads to a small variation of Γ for 1-butanol, which is a strong indication of the formation of a stable monolayer.²¹ On the other hand, it leads to a continuous increase of Γ for acetic acid due to the adsorption of an increasing amount of molecules at the ice surface up to the completion of the layer, occurring just before the condensation occurs (this condensation is indicated by the sudden vertical jump of the isotherm). Further, in the intermediate pressure range of about $10^{-2} - 1$ Pa, the number of adsorbed alcohol molecules is always larger than that of acetic acid.

The simulated isotherms, calculated at 233 K, agree nicely with the experimental ones, measured at 228 K,²⁶ especially in the low pressure range and for 1-butanol (see Figure 1a). At larger coverage, the agreement is less satisfactory for these alcohol molecules, although the large dispersion of the experimental data makes the comparison with the simulation results not so easy. As previously discussed,²¹ this slight discrepancy could come from an underestimation of the lateral interactions between alcohol molecules with the AUA4 potential model, especially when long aliphatic chains are involved. Also, our simulations seem to somewhat overestimate the amount of adsorbed acetic acid molecules in the whole pressure range (Fig-

ure 1b), a feature that could come from a slight overestimation of the interaction between the COOH group and the ice surface, when using the AUA4 model. Nevertheless, it is very satisfying to see that the subtle balance between adsorbate-ice and adsorbate-adsorbate interactions, which governs the adsorption process, can be reproduced quite well by using a simple combination of empirical models originally parametrized for pure compounds only.

Properties of the adsorbed molecules

As in our previous work,²¹ the analysis of these results has been performed in terms of number density profile, adsorption energy, and orientation of the adsorbed molecules (some of the corresponding curves are provided as Supplementary Information, in addition to those given below). This analysis allows us to draw the following conclusions on the individual adsorption of the two species at 233 K.

At the low surface coverage corresponding to the pressure value of 0.003 Pa, the distribution of the molecular C–C axis orientations ($P(\cos\theta_1)$) for the 1-butanol molecules (see Figure 2a) is characterized by a broad peak, the maximum of which corresponds to the value of $\theta_1 \sim 105^\circ$. This indicates that the 1-butanol molecules are adsorbed with their molecular axis being slightly (by about 25°) tilted with respect to the ice surface, the OH group being closer to the water molecules than the methyl group. This configuration is very similar to that obtained at 228 K.²¹ The distribution of the interaction energy between one adsorbed 1-butanol molecule and the ice surface, U_{alc-w} , exhibits only one, broad, peak, the maximum of which corresponds to about -67 kJ.mol^{-1} (Figure 2c), in a nice agreement with the experimental value of the adsorption energy of $-67.8 \pm 3.8 \text{ kJ.mol}^{-1}$, measured at very low coverage.²⁶ Meanwhile, the distribution of the interaction energy of one adsorbed 1-butanol molecule with the rest of the adsorption layer, $U_{alc-alc}$, also exhibits one single peak, the maximum of which corresponding to a small value close to zero energy, indicating that the lateral interaction between the adsorbed alcohol molecules is very weak in this low pressure range (Figure 2e). By contrast, at pressures corresponding to saturation coverage

of the ice surface, most of the adsorbed molecules tend to move their apolar tail away from, and pointing their polar head towards the ice surface, their molecular axis now being almost perpendicular to the surface, as indicated by the main peak of the distribution $P(\cos\theta_1)$ around the value of $\cos\theta_1 = -0.9$ (Figure 2b). For simplicity of the following discussions, this orientation will be referred as orientation Alc_A . In this new orientation, the U_{alc-w} and $U_{alc-alc}$ distributions of the interaction energies have their maximum around -44 kJ.mol^{-1} (Figure 2d) and -57 kJ.mol^{-1} (Figure 2f), respectively, indicating a strong increase of the lateral interactions between the adsorbed 1-butanol molecules at the expense of their interaction with ice. It is, however, worth noting that a few adsorbed 1-butanol molecules may also stay almost flat on the surface at this high coverage, as shown by the small peak around $\cos\theta_1 = 0$ in Figure 2b (below, this orientation will be referred to as orientation Alc_B). As an illustration, snapshots of the 1-butanol/ice system are given on Figure 3 at low (Figure 3a) and saturation (Figure 3b) coverages of the ice surface, in which two molecules exhibiting orientations Alc_A and Alc_B are indicated.

When considering the acetic acid molecules, the analysis of the simulation results in the low pressure range, when only a few molecules are adsorbed at the ice surface, indicates that all these molecules adopt almost the same alignment, as indicated by the large peak in $P(\cos\theta_1)$ between -0.85 and -0.65 (Figure 4a). In this configuration (referred to as orientation Ac_α), the C-C axis of the acetic acid molecule is tilted by about $30\text{--}50^\circ$ from the surface normal, the carboxyl group pointing to the water molecules. The corresponding distribution of the interaction energy between one adsorbed acetic acid molecule and the ice phase, U_{ac-w} , is characterized by one single peak, around -73 kJ.mol^{-1} (Figure 4c). In this situation, the lateral interaction between adsorbed acetic acid molecules is vanishingly small (Figure 4e), indicating that the adsorbed molecules stay isolated from each other. Note that the obtained value of U_{ac-w} agrees well with the experimental value of $-73.1 \pm 11.7 \text{ kJ.mol}^{-1}$.²⁶ These conclusions remain valid at larger pressures, in the region where the adsorption isotherm slope changes, as indicated by the analysis of the simulation data

performed at the pressure of 0.02 Pa. In particular, there is still only one single peak in the $P(\cos\theta_1)$ and $P(U_{ac-w})$ distributions, which can be unambiguously related to configuration Ac_α .

On the contrary, the analysis of the results obtained at higher pressures, just below the point of condensation, indicates the preference for two different orientations, as evidenced from the two peaks in the $P(\cos\theta_1)$ distribution of the molecular C–C axis orientations (Figure 4b). It should also be noted that, consistently with this picture, the corresponding energy distributions exhibit two separate peaks (Figures 4d and 4f). The first of these orientations is, in fact, very similar to Ac_α , observed also at low coverage, while in the second orientation (referred to as orientation Ac_β) the molecular C–C axis lies more or less parallel to the ice surface. This new orientation, Ac_β , can thus be associated with the second peak of the U_{ac-w} distribution, occurring at -38 kJ.mol^{-1} , while the first peak at -68 kJ.mol^{-1} is still associated with Ac_α . The distribution of the lateral interactions, U_{ac-ac} , has its maxima at -22 kJ.mol^{-1} (orientation Ac_α) and -45 kJ.mol^{-1} (orientation Ac_β), indicating that these two orientations differ not only in the interaction with the water molecules, but also in that with the surrounding adsorbed molecules. These results can thus be related to the existence of two preferred adsorption configurations at the ice surface for the acetic acid molecules, as previously evidenced for formic acid molecules.²⁷ The first one, at which acetic acid molecules adopt orientations Ac_α , is preferentially evidenced at low surface coverage, i.e., at the low pressure range (Figure 5a). At higher coverages, additional adsorption configuration of a different type is also adopted by the acetic acid molecules, characterized by the orientation Ac_β (Figure 5b).

When the gas phase contains a mixture of 1-butanol and acetic acid molecules, the corresponding simulated adsorption isotherms (blue and green curves in Figure 1) overlap with those of the non-mixed species in the very low pressure range, indicating that the adsorbed molecules of one species are not significantly influenced by those of the other species, when the total number of adsorbed molecules remains quite weak (low coverage of the ice

surface). This is confirmed, for instance, by the analysis of the orientational distributions $P(\cos\theta_1)$ (Figure 6a and 6b) which do not show any strong difference at different gas phase compositions.

The situation is clearly different when the pressure increases. Indeed, the adsorption isotherms for the mixtures all show a plateau, for both molecules at higher pressures (blue and green curves in Figure 1), indicating that, before the condensation occurs, one molecular adsorbed layer is stabilized at the surface of ice in a broad range of pressures.⁵ Moreover, although this monolayer contains co-adsorbed 1-butanol and acetic acid molecules, it is characterized by a significantly lower number of both species than in the non-mixed situation at similar pressures. This shows that the 1-butanol and acetic acid molecules indeed compete for being adsorbed at the surface.

It is worth noting that the simulated behavior of the mixtures agrees, in general, well with the experimental results (grey symbols on Figures 1e and 1f). This agreement is even quantitative when the gas phase contains 25 % of 1-butanol, as evidenced in Figure 1e. On the other hand, the agreement is only qualitative when the gas mixture contains 38 % of acetic acid, as here the simulation results overestimate the amount of adsorbed acetic acid molecules, as already observed also in the non-mixed case. In any case, when the two species can simultaneously be trapped at the ice surface, the maximum number of both molecules that can be adsorbed at the surface is considerably less than in the corresponding non-mixed situations, in accordance with the experimental observations.

To understand the situation more deeply, the distributions of molecular orientations at the ice surface have thus been analyzed at saturation coverage (corresponding to the pressure of 1 Pa), just before the occurrence of the condensation. The corresponding curves are shown in the bottom row of Figure 6, for the mixed (blue and green curves) and non-mixed (red curves) systems (given for reference). These distributions clearly show that, within the mixed adsorbed layer, preference for orientation Ac_β nearly vanishes and, as a consequence, acetic acid molecules preferentially adopt orientation Ac_α . The situation is somewhat more

balanced for 1-butanol, as both orientations Alc_A and Alc_B are still evidenced when the alcohol molecules are co-adsorbed with acetic acid. However, it is clear that the higher the concentration of 1-butanol is at the ice surface, the weaker is their preference for orientation Alc_B . In addition, the surface distribution of the XY positions of the carbon atom to which the alcoholic or acidic functional group is attached has been calculated for both species in 10,000 equilibrium sample configurations, and superimposed in the same graph, shown in Figure 7, for both gas mixtures considered. First, as evidenced by the various spots on these spatial distributions, the entire surface is covered by the adsorbed molecules, a feature which could be related to the plateau observed in the corresponding adsorption isotherms (Figures 1c and d). Further, 1-butanol and acetic acid molecules clearly prefer to occupy well-defined adsorption positions on the ice surface. It is also seen that the two species are not fully mixed at the ice surface, instead they tend to form well-separated self-aggregates of the same species. Snapshots taken from the simulations are given in Figure 8, to illustrate the orientational configurations adopted by the 1-butanol and acetic acid molecules in the mixed adsorption layers at the ice surface, at low and saturation coverages.

Selectivity of the adsorption process

The spatial distributions shown in Figure 7 also suggest that the composition of the adsorption layer is different from that of the gas phase, due to the competition in the adsorption process between the 1-butanol and acetic acid molecules. This difference can be more quantitatively characterized by calculating the selectivity of the ice surface for 1-butanol with respect to acetic acid, defined as^{12,28}

$$\alpha_{\text{C}_4\text{H}_{10}\text{O}/\text{C}_2\text{H}_4\text{O}_2} = \frac{N_{\text{C}_4\text{H}_{10}\text{O}}/N_{\text{C}_2\text{H}_4\text{O}_2}}{y_{\text{C}_4\text{H}_{10}\text{O}}/y_{\text{C}_2\text{H}_4\text{O}_2}} \quad (1)$$

where N_j represents the molar fraction of species j ($j = \text{C}_4\text{H}_{10}\text{O}$ or $\text{C}_2\text{H}_4\text{O}_2$) in the adsorption layer, while y_j is the corresponding molar fraction in the gas phase. Thus, following the

definition given by Eq. 1, values of $\alpha_{\text{C}_4\text{H}_{10}\text{O}/\text{C}_2\text{H}_4\text{O}_2}$ larger than 1 indicate that the relative proportion of 1-butanol with respect to acetic acid is larger at the ice surface than in the gas phase, i.e., the adsorption process is selective for 1-butanol. By contrast, $\alpha_{\text{C}_4\text{H}_{10}\text{O}/\text{C}_2\text{H}_4\text{O}_2}$ values smaller than 1 indicate that the adsorption process is selective for acetic acid.

As shown in Figure 9, the adsorption process remains always selective in favor of the acetic acid molecules (i.e., $\alpha_{\text{C}_4\text{H}_{10}\text{O}/\text{C}_2\text{H}_4\text{O}_2} < 1$) when 1-butanol molecules are in majority (i.e., 62 %) in the gas phase (green symbols). Nevertheless, it should be noted that the fraction of 1-butanol at the surface increases with pressure up to saturation, as indicated by the increase of $\alpha_{\text{C}_4\text{H}_{10}\text{O}/\text{C}_2\text{H}_4\text{O}_2}$ up to a more or less constant value. This behavior is even more pronounced for the other mixture considered here (25 % of 1-butanol). Indeed, in this case, the value of $\alpha_{\text{C}_4\text{H}_{10}\text{O}/\text{C}_2\text{H}_4\text{O}_2}$ remains lower than 1 only up to a threshold pressure, above which the adsorption process, initially being selective for acetic acid, becomes progressively more favorable to the alcohol molecules, as indicated by the selectivity values larger than 1 at higher pressures. Note that the threshold pressure at which the selectivity becomes larger than 1 roughly corresponds to the pressure at which the adsorption isotherms start to exhibit a plateau (i.e., when a more or less saturated mixed monolayer is formed at the surface).

Conclusions

Summarizing, the results of this first GCMC simulations devoted to the characterization of competitive adsorption clearly show that the trapping of acetic acid molecules is favored at the surface of ice with respect to that of 1-butanol at low pressures, irrespective of the gas phase composition, in a clear accordance with earlier experimental findings.⁸ By contrast, at higher pressures, more 1-butanol molecules can be adsorbed on the expense of the adsorption of the acetic acid molecules, preventing the acetic acid molecules from adopting orientation Ac_β . Moreover, the adsorption process leads to a gradual increase of the 1-butanol mole fraction in the adsorption layer with respect to that in the mixed gas phase, as shown by

the increasing value of the ice selectivity for 1-butanol. Similar conclusions are obtained at the two temperatures considered, i.e., 228 K and 233 K. The present results clearly point out that interactions between co-adsorbing gases can play a significant role in their trapping on atmospheric ice particles, and modify their relative molar fractions, especially in the saturated portion of the adsorption isotherm, as already observed in the experiments. Further, they underline that competitive adsorption effects cannot be disregarded when considering real atmospheric situations. The present study also shows that the GCMC method is a powerful and versatile tool for characterizing this competition, provided that accurate interaction potential models are available.

Conflicts of interest

There are no conflicts to declare.

Supporting Information

Includes information on the NPT simulations performed for the conversion between chemical potentials and pressures (Widom procedure, see also Ref.^{13,21,24}), and additional results on the structural and orientational analyses performed to better understand the behavior of the molecules adsorbed at the surface of ice.

Acknowledgements

The Region Bourgogne Franche-Comté is gratefully acknowledged for its financial support through the grant PASCOA 2020-0052. Computations have been performed using resources of the Mésocentre de calcul de Franche-Comté. PJ acknowledges financial support from the Hungarian NKFIH Foundation under Project No. 134596. The license to use the GIBBS software has been granted under the contractual letter ref. IFPEN n° 2020-0744.

References

- (1) Dominé, F.; Shepson, P. Air-Snow Interactions and Atmospheric Chemistry. *Science* **2002**, *297*, 1506–1510.
- (2) Abbatt, J. Interactions of Atmospheric Trace Gases With Ice Surfaces: Adsorption and Reaction. *Chem. Rev.* **2003**, *103*, 4783–4800.
- (3) Huthwelker, T.; Ammann, M.; Peter, T. The Uptake of Acidic Gases on Ice. *Chem. Rev.* **2006**, *106*, 1375–1444.
- (4) McNeill, V. F.; Grannas, A.; Abbatt, J.; Ammann, M.; Ariya, P.; Bartels-Rausch, T.; Dominé, F.; Donaldson, D.; Guzman, M.; Heger, D. et al. Organics in Environmental Ices: Sources, Chemistry, and Impacts. *Atmospheric Chemistry and Physics* **2012**, *12*, 9653–9678.
- (5) Picaud, S.; Jedlovszky, P. Molecular-Scale Simulations of Organic Compounds on Ice: Application to Atmospheric and Interstellar Sciences. *Molecular Simulation* **2019**, *45*, 403–416.
- (6) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Oxford university press, 2017.
- (7) Jedlovszky, P.; Partay, L.; Hoang, P.; Picaud, S.; von Hessberg, P.; Crowley, J. Determination of the Adsorption Isotherms of Methanol on the Surface of Ice. An Experimental and Grand Canonical Monte Carlo Simulation Study. *J. Am. Chem. Soc.* **2006**, *128*, 15300–15308.
- (8) Sokolov, O.; Abbatt, J. Competitive Adsorption of Atmospheric Trace Gases Onto Ice at 228 K: HNO₃/HCl, 1-Butanol/Acetic acid and 1-Butanol/HCl. *Geophysical research letters* **2002**, *29*, 32.

- (9) Von Hessberg, P.; Pouvesle, N.; Winkler, A.; Schuster, G.; Crowley, J. Interaction of Formic and Acetic Acid with Ice Surfaces Between 187 and 227 K. Investigation of Single Species- and Competitive Adsorption. *Physical Chemistry Chemical Physics* **2008**, *10*, 2345–2355.
- (10) Lectez, S.; Simon, J.-M.; Mousis, O.; Picaud, S.; Altwegg, K.; Rubin, M.; Salazar, J. A 32–70 K Formation Temperature Range for the Ice Grains Agglomerated by Comet 67 P/Churyumov–Gerasimenko. *The Astrophysical Journal Letters* **2015**, *805*, L1.
- (11) Patt, A.; Simon, J.-M.; Picaud, S.; Salazar, J. A Grand Canonical Monte Carlo Study of the N₂, CO, and Mixed N₂–CO Clathrate Hydrates. *The Journal of Physical Chemistry C* **2018**, *122*, 18432–18444.
- (12) Petuya, C.; Patt, A.; Simon, J.-M.; Picaud, S.; Salazar, J.; Desmedt, A. Molecular Selectivity of CO–N₂ Mixed Hydrates: Raman Spectroscopy and GCMC Studies. *The Journal of Physical Chemistry C* **2020**, *124*, 11886–11891.
- (13) Patt, A.; Picaud, S. Molecular Selectivity of CH₄–C₂H₆ Mixed Hydrates: A GCMC Study. *ACS Earth and Space Chemistry* **2021**, *5*, 1782–1791.
- (14) Cavalli, F.; Geiger, H.; Barnes, I.; Becker, K. FTIR Kinetic, Product, and Modeling Study of the OH-Initiated Oxidation of 1-Butanol in Air. *Environmental science & technology* **2002**, *36*, 1263–1270.
- (15) Andersen, V.; Wallington, T.; Nielsen, O. Atmospheric Chemistry of i-Butanol. *The Journal of Physical Chemistry A* **2010**, *114*, 12462–12469.
- (16) Khan, M.; Lyons, K.; Chhantyal-Pun, R.; McGillen, M.; Caravan, R.; Taatjes, C.; Orr-Ewing, A.; Percival, C.; Shallcross, D. Investigating the Tropospheric Chemistry of Acetic Acid Using the Global 3-D Chemistry Transport Model, STOCHEM-CRI. *Journal of Geophysical Research: Atmospheres* **2018**, *123*, 6267–6281.

- (17) Abascal, J.; Sanz, E.; García Fernández, R.; Vega, C. A Potential Model for the Study of Ices and Amorphous Water: TIP4P/Ice. *The Journal of chemical physics* **2005**, *122*, 234511.
- (18) Conde, M.; Rovere, M.; Gallo, P. High Precision Determination of the Melting Points of Water TIP4P/2005 and Water TIP4P/Ice Models by the Direct Coexistence Technique. *The Journal of chemical physics* **2017**, *147*, 244506.
- (19) Ferrando, N.; Lachet, V.; Teuler, J.-M.; Boutin, A. Transferable Force Field for Alcohols and Polyalcohols. *The Journal of Physical Chemistry B* **2009**, *113*, 5985–5995.
- (20) Ferrando, N.; Gedik, I.; Lachet, V.; Pigeon, L.; Lugo, R. Prediction of Phase Equilibrium and Hydration Free Energy of Carboxylic Acids by Monte Carlo Simulations. *The Journal of Physical Chemistry B* **2013**, *117*, 7123–7132.
- (21) Joliat, J.; Picaud, S.; Patt, A.; Jedlovsky, P. Adsorption of C2–C5 Alcohols on Ice: A Grand Canonical Monte Carlo Simulation Study. *The Journal of Chemical Physics* **2022**, *156*, 224702.
- (22) Frenkel, D.; Smit, B. *Understanding Molecular Simulation: From Algorithms to Applications*; Elsevier, 2001; Vol. 1.
- (23) Ungerer, P.; Tavitian, B.; Boutin, A. *Applications of Molecular Simulation in the Oil and Gas Industry: Monte Carlo Methods*; Editions Technip, 2005.
- (24) Joliat, J.; Patt, A.; Simon, J. M.; Picaud, S. Adsorption of Organic Compounds at the Surface of Enceladus’ Ice Grains. A Grand Canonical Monte Carlo Simulation Study. *Molecular Simulation* **2022**, *48*, 19–30.
- (25) Rohatgi, A. Webplotdigitizer: Version 4.5. 2021; <https://automeris.io/WebPlotDigitizer> (date of access : June, 08, 2023).

- (26) Sokolov, O.; Abbatt, J. Adsorption to Ice of n-Alcohols (Ethanol to 1-Hexanol), Acetic Acid and Hexanal. *J. Phys. Chem. A* **2002**, *106*, 775–782.
- (27) Jedlovszky, P.; Hantal, G.; Neuróhr, K.; Picaud, S.; Hoang, P.; Von Hessberg, P.; Crowley, J. Adsorption Isotherm of Formic Acid on the Surface of Ice, as Seen From Experiments and Grand Canonical Monte Carlo Simulation. *The Journal of Physical Chemistry C* **2008**, *112*, 8976–8987.
- (28) Guo, Y.; Zeng, Z.; Li, L.; Su, C.; Chen, R.; Wang, C.; Zhou, K.; Xu, X.; Li, H. Competitive Adsorption of Methanol–Acetone on Surface Functionalization (- COOH,- OH,- NH₂, and- SO₃H): Grand Canonical Monte Carlo and Density Functional Theory Simulations. *ACS applied materials & interfaces* **2019**, *11*, 34241–34250.

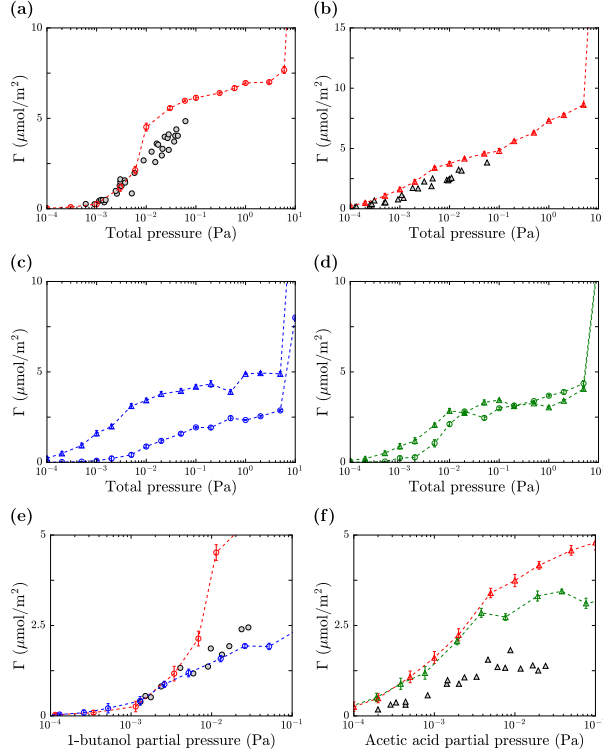


Figure 1: Average number of 1-butanol (circles) and acetic acid (triangles) molecules adsorbed on ice as a function of the pressure (note that the errors bars are smaller than the symbols), as calculated from the present GCMC simulations at 233 K, for various proportions of these two species in the gas phase. Top row: Red curves represent the results obtained for the neat (non mixed) systems. Middle row: Results obtained for the gas phase 1-butanol:acetic acid molar ratios of 25:75 (blue curves) and of 62:38 (green curves). Bottom row : Comparison between results obtained for the non-mixed and the mixed systems, for 1-butanol (left) and acetic acid (right) molecules. Lines connecting the points are only guides to the eye. Comparisons with the experimental data⁸ are shown as grey symbols. Note that for the mixtures, these experimental data are available for only one species in each case, i.e., 1-butanol for the gas phase 1-butanol:acetic acid molar ratios of 25:75, and acetic acid for the gas phase 1-butanol:acetic acid molar ratios of 62:38.

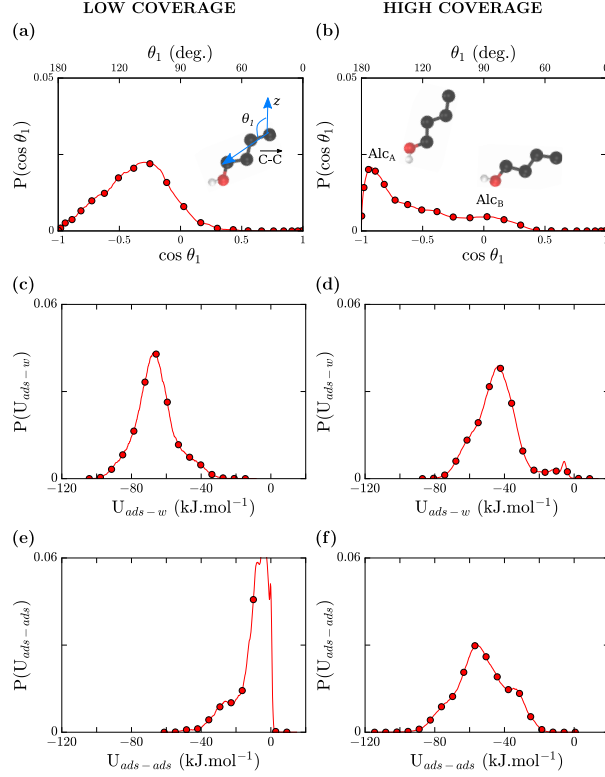


Figure 2: Top row : Distributions of the molecular orientations of the adsorbed 1-butanol molecules for the neat (non mixed) system. Insets show the definition of the θ_1 angle and, also, examples of the preferential orientations (Alc_A and Alc_B) adopted by the 1-butanol molecules at the ice surface (see text for more explanation). In these representations of the molecules, red, white, and black (gray) circles represent oxygen, hydrogen and carbon atoms, respectively. Note that hydrogen atoms of the aliphatic chains are not shown for clarity. Middle and bottom rows : Distribution of the interaction energy of an adsorbed 1-butanol molecule with the ice phase $P(U_{ads-w})$ and with the other adsorbed molecules $P(U_{ads-ads})$. All these analyses have been performed at 233 K and at pressure values of 0.003 Pa (low coverage, left hand side of the figure) and 1 Pa (saturation coverage, right hand side).

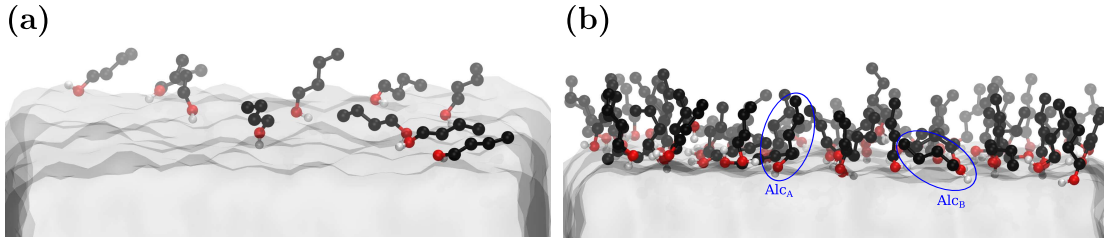


Figure 3: Snapshots taken from the simulations at (a) low and (b) saturation coverages for the 1-butanol molecules adsorbed on ice, at 233 K. Two molecules exhibiting the typical orientations Alc_A and Alc_B adopted by the 1-butanol species at the saturation coverage of the ice surface are indicated in blue, as an illustration. In these snapshots of the molecules, red, white, and black (gray) circles represent oxygen, hydrogen and carbon atoms, respectively. Note that hydrogen atoms of the aliphatic chains are not shown for clarity. The ice crystal has been drawn as a continuous grey material.

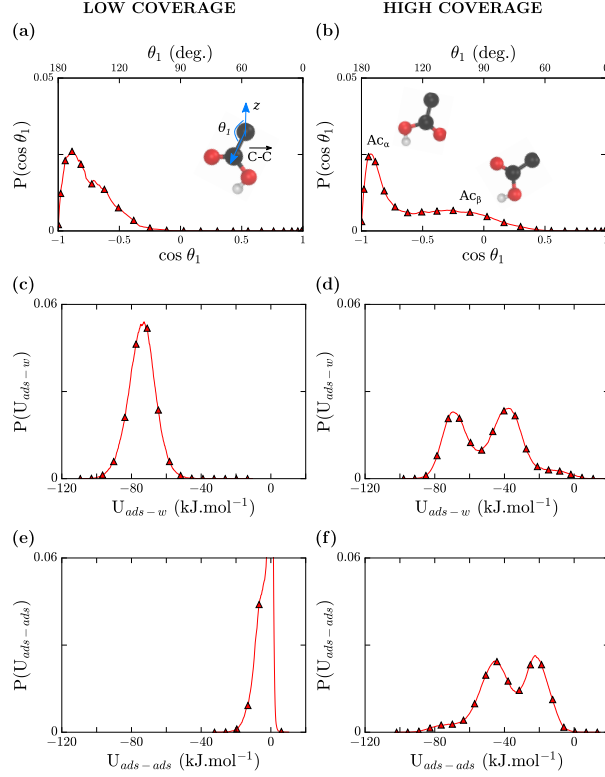


Figure 4: Top row : Distributions of the molecular orientations of the adsorbed acetic acid molecules for the neat (non mixed) system. Insets show the definition of the θ_1 angle and, also, examples of the preferential orientations (Ac_α and Ac_β) adopted by the acetic acid molecules at the ice surface (see text for more explanation). In these representations of the molecules, red, white, and black (gray) circles represent oxygen, hydrogen and carbon atoms, respectively. Note that hydrogen atoms of the aliphatic chains are not shown for clarity. Middle and bottom rows : Distribution of the interaction energy of an adsorbed acetic acid molecule with the ice phase $P(U_{ads-w})$ and with the other adsorbed molecules $P(U_{ads-ads})$. All these analyses have been performed at 233 K and at pressure values of 0.0005 Pa (low coverage, left hand side of the figure) and 1 Pa (saturation coverage, right hand side).

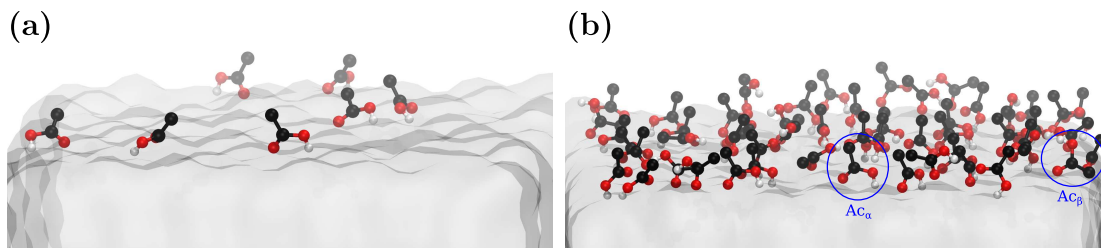


Figure 5: Snapshots taken from the simulations at (a) low and (b) saturation coverages for the acetic acid molecules adsorbed on ice, at 233 K. Two molecules exhibiting the typical orientations Ac_{α} and Ac_{β} adopted by the acetic acid species at the saturation coverage of the ice surface are indicated in blue, as an illustration. In these snapshots of the molecules, red, white, and black (gray) circles represent oxygen, hydrogen and carbon atoms, respectively. Note that hydrogen atoms of the aliphatic chains are not shown for clarity. The ice crystal has been drawn as a continuous grey material.

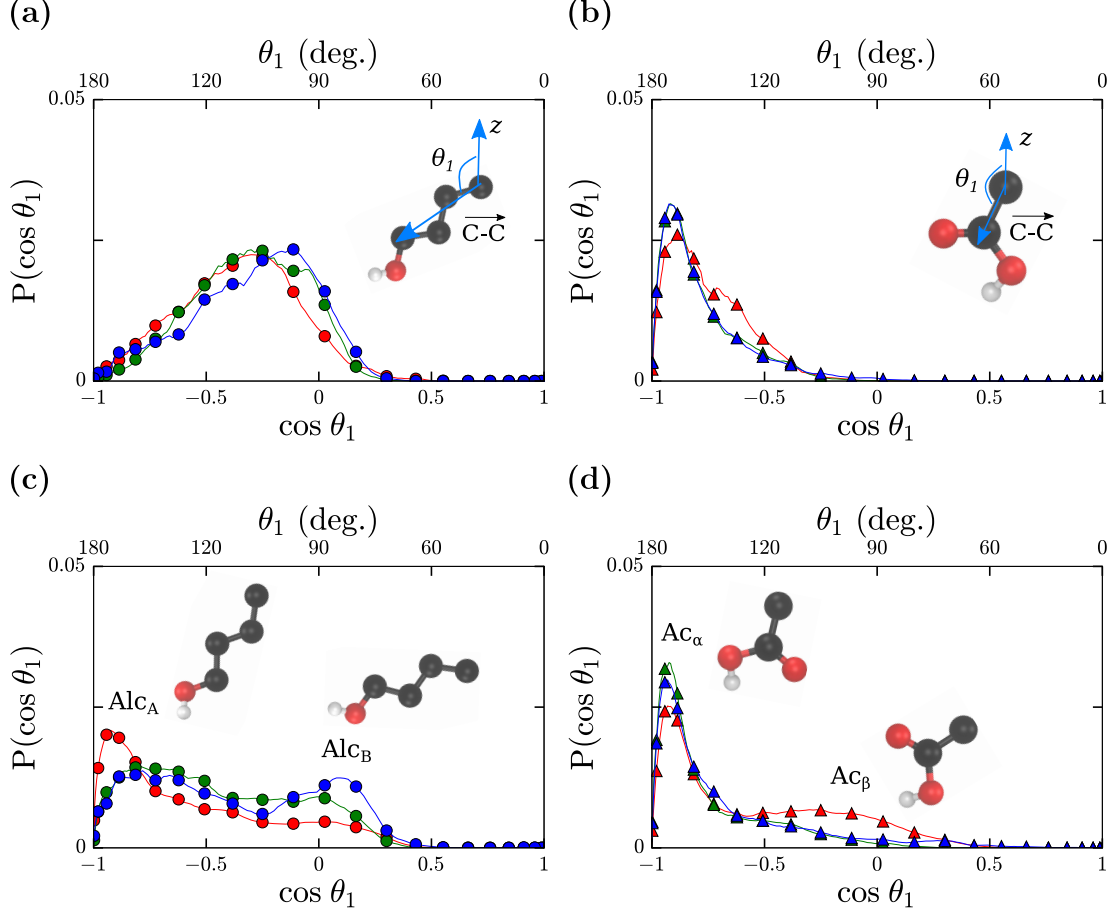
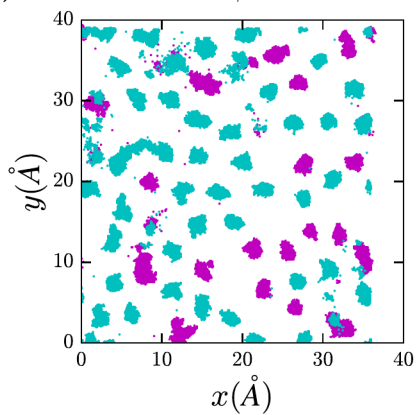


Figure 6: Distributions of the molecular orientations of the adsorbed 1-butanol (left) and acetic acid (right) molecules, for the neat (i.e., non mixed) systems (red curves) and for 1-butanol:acetic acid gas phase molar ratios of 62:38 (green curves) and 25:75 (blue curves). Top and bottom rows correspond to low and saturation coverages of the ice surface by the adsorbate, respectively. Insets show the definition of the θ_1 angle. The preferential orientations for the 1-butanol (Alc_A and Alc_B), and for the acetic acid (Ac_α and Ac_β) molecules are also indicated (see text for more explanation). In these representations of the molecules, red, white, and black (gray) circles represent oxygen, hydrogen and carbon atoms, respectively. Note that hydrogen atoms of the aliphatic chains are not shown for clarity.

(a) 25% 1-butanol / 75% acetic acid



(b) 62% 1-butanol / 38% acetic acid

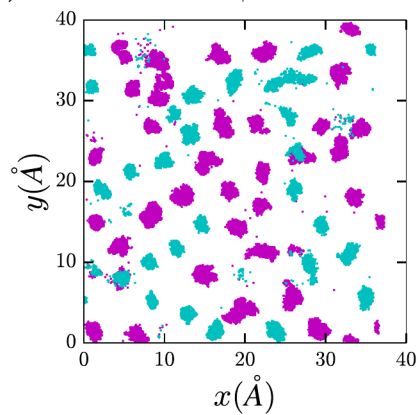
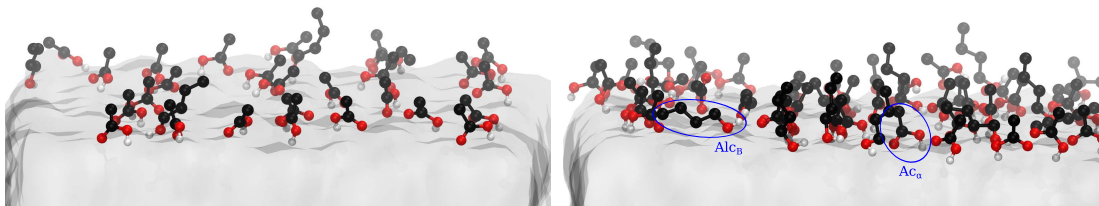


Figure 7: Surface distribution of the XY positions of the carbon atom of the 1-butanol (purple dots) and acetic acid (blue dots) molecules to which the functional group is attached, at saturation coverages of the ice surface, and for the two compositions of the mixed gas phase investigated here.

(a) 25% 1-butanol / 75% acetic acid



(b) 62% 1-butanol / 38% acetic acid

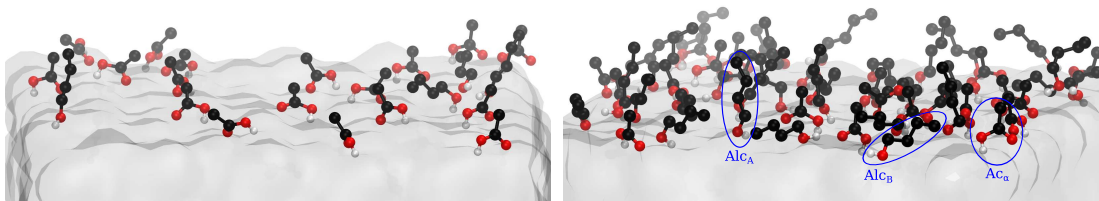


Figure 8: Snapshots taken from the simulations of mixtures of 1-butanol and acetic acid molecules adsorbed on ice, at 233 K and at low (left hand side) and saturation (right hand side) coverages. Typical orientations adopted by the adsorbed species at the ice surface (see text) are indicated in blue, as an illustration. In these snapshots of the molecules, red, white, and black (gray) circles represent oxygen, hydrogen and carbon atoms, respectively. Note that hydrogen atoms of the aliphatic chains are not shown for clarity. The ice crystal has been drawn as a continuous grey material.

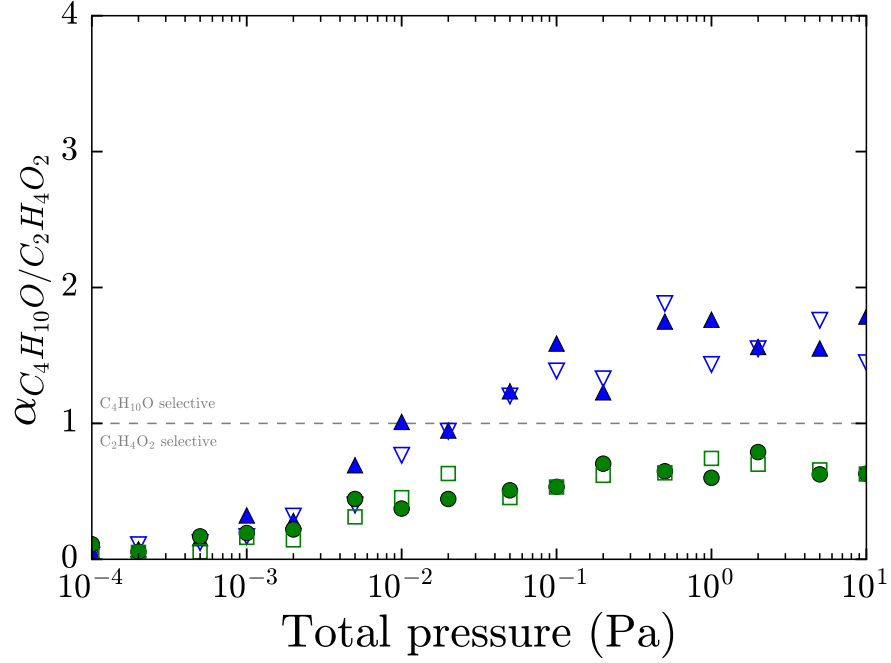
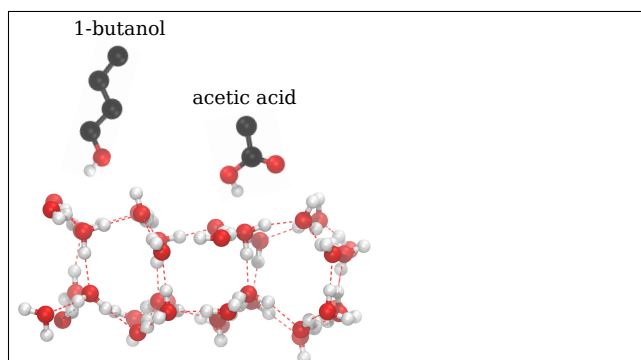


Figure 9: Selectivity of the ice surface as a function of the total pressure, as defined by Eq. 1. Results have been calculated at 228 K (open symbols) and 233 K (full symbols), for the gas phase 1-butanol:acetic acid molar ratio of 62:38 (green symbols) and 25:75 (blue symbols). The limit between acetic acid and 1-butanol selective ice surfaces, corresponding to the selectivity value of 1, is indicated by the horizontal dashed line.

TOC Graphic



Supporting information

Competitive Adsorption of Trace Gases on Ice at Tropospheric Temperatures : A Grand Canonical Monte Carlo Simulation Study

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S1. NPT simulation details

To determine a consistent and accurate relation between pressure and chemical potential, we have performed a series of Monte Carlo simulations in the (N,P,T) ensemble, over the same ranges of pressure and temperature than in the GCMC simulations, in a cubic box (of side 3.10^4 Å) containing 300 molecules (with varying proportions of each species depending on the simulated gas phase mixture). In these simulations, the molecules have been subjected not only to translation and rotation MC moves but also to changes in their internal configuration. In addition, identity exchange move have been considered in the case of mixtures, allowing exchange of positions of two randomly selected molecules. These four moves have been performed with equal probabilities of 24% each. The system as a whole has also been subjected to the volume change move, with a 4% probability. Once the systems have reached equilibrium after a total of 10^8 Monte Carlo steps, the Widom insertion test phase took place over an additional 10^8 Monte Carlo steps, with probabilities of Monte Carlo movements during this phase set at 15% for translation and for rotation, 15% for internal configuration change, 15% for identity exchange, 1% for volume change, and 39% for insertion tests. Note that the interactions between the molecules have been calculated using the same models than in the GCMC simulations, with cut-offs equal to half the size of the simulation box. Then, the conversion between chemical potential and pressure has been achieved as in our previous works.[1–3]

S2. Additional Figures

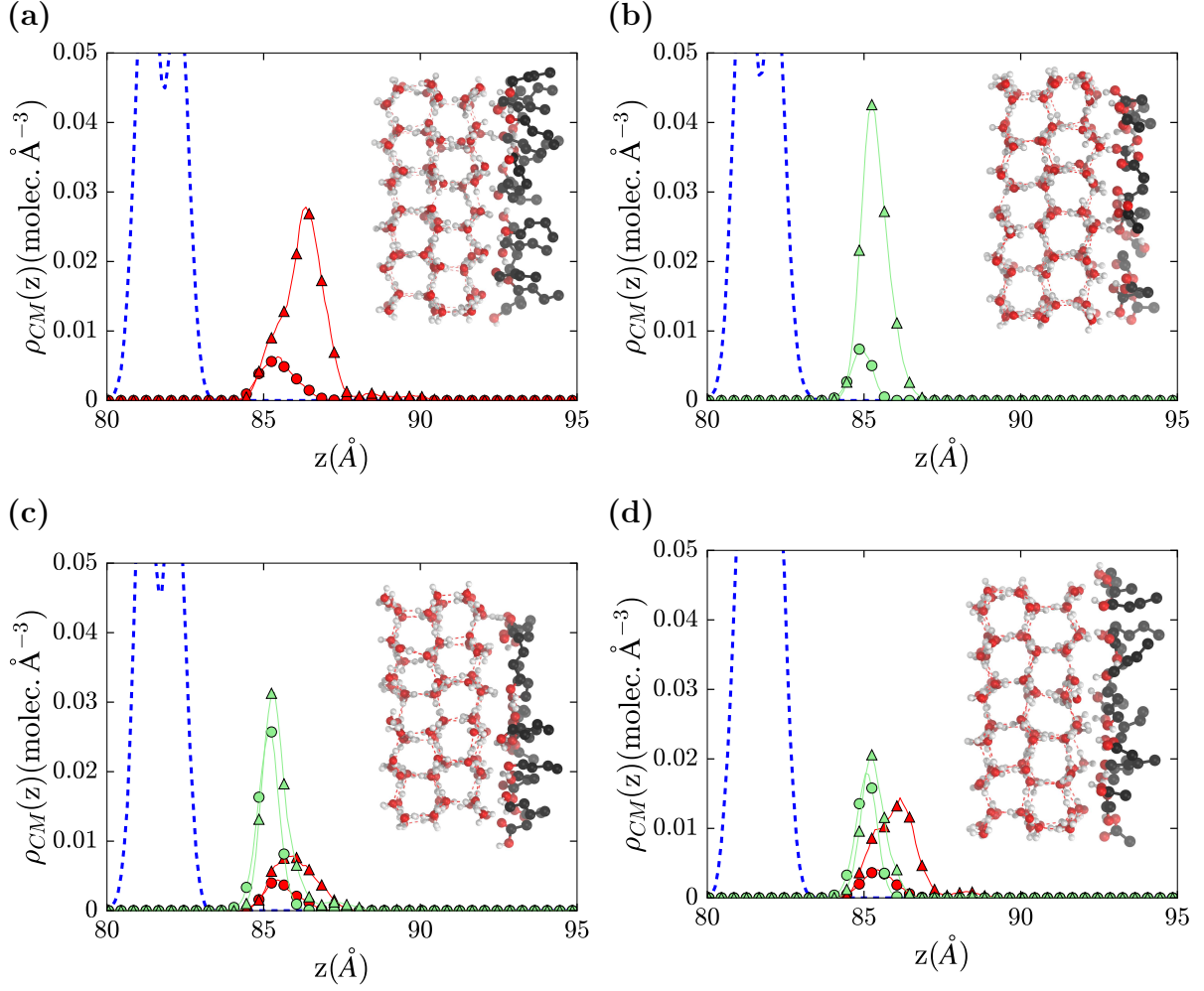


Figure S1: Number density profiles for 1-butanol and acetic acid centers of mass, as obtained from the simulations of non-mixed systems ((a) and (b)) and of (c) 25:75 and (d) 62:38 mixtures, at 233 K. The results are given at low (circles) and saturation (triangles) coverages of the ice surface, and for the 1-butanol (red curves) and acetic acid (green curves) molecules. Note that the analysis at saturation coverage has been performed at the pressure of 1 Pa in each case, whereas at lower coverage, the analysis has been performed at pressures depending on the system under investigation, the number of adsorbed molecules having to be large enough for statistical relevance. The corresponding values of the chosen pressures are $P = 3 \times 10^{-3}$ Pa and $P = 5 \times 10^{-4}$ Pa for neat 1-butanol and neat acetic acid systems, respectively, and $P = 10^{-2}$ Pa for the 25:75, and $P = 5 \times 10^{-3}$ Pa for the 62:38 mixtures, respectively. For reference, the outer tail of the number density profile of the water centers of mass is also given (dashed blue line). In addition, snapshots issued from the simulations at saturation coverages are given, to illustrate the adsorption geometry when the molecules form a monolayer at the ice surface. In these snapshots, red, white, and black (gray) circles represent oxygen, hydrogen and carbon (bottom carbon) atoms, respectively. Note that hydrogen atoms of the aliphatic chains are not explicitly included in the united atom AUA4 potential model and, thus, they are not shown.

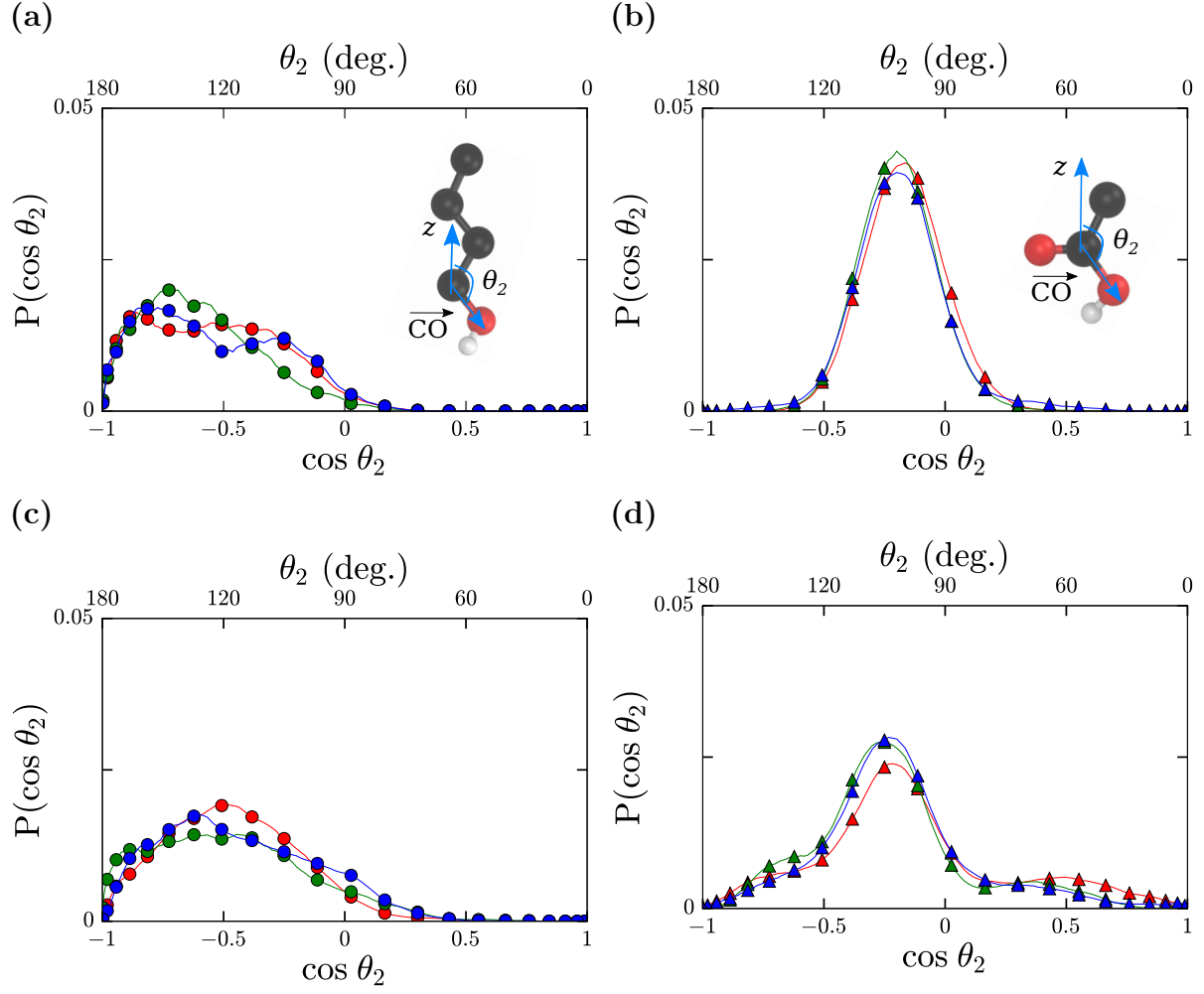


Figure S2: Distribution of the molecular angle θ_2 formed between the CO vector and the normal z to the ice surface (as illustrated by the inserts), for 1-butanol (left) and acetic acid (right) molecules adsorbed on ice at low (top row) and saturation (bottom row) coverages of the ice surface. The results for the non-mixed systems are given in red, whereas blue and green curves represent the results obtained for the 25:75 and 62:38 mixed systems, respectively.

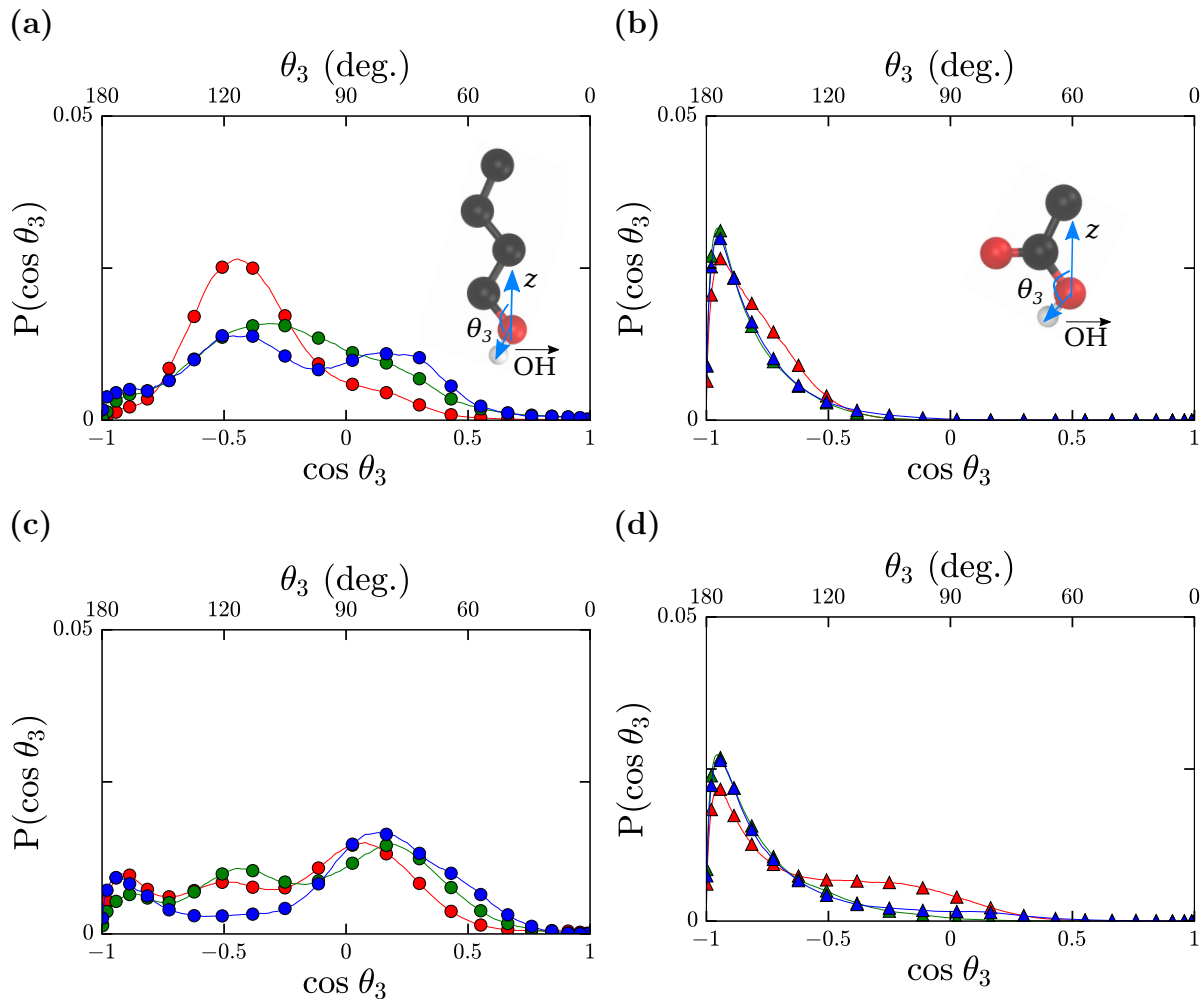


Figure S3: Distribution of the molecular angle θ_3 formed between the OH vector and the normal z to the ice surface (as illustrated by the inserts), for 1-butanol (left) and acetic acid (right) molecules adsorbed on ice at low (top row) and saturation (bottom row) coverages of the ice surface. The results for the non-mixed systems are given in red, whereas blue and green curves represent the results obtained for the 25:75 and 62:38 mixed systems, respectively.

References

- [1] A Patt and S Picaud. “Molecular Selectivity of CH_4 – C_2H_6 Mixed Hydrates: A GCMC Study”. In: *ACS Earth and Space Chemistry* 5.7 (2021), pp. 1782–1791.
- [2] J. Joliat et al. “Adsorption of C2-C5 Alcohols on Ice. A Grand Canonical Monte Carlo Simulation Study”. In: *The Journal of Chemical Physics* 156 (2022), p. 224702.
- [3] Julien Joliat, Théo Lenoir, and Sylvain Picaud. “Comparative Study of the Adsorption of 1-and 2-Propanol on Ice by Means of Grand Canonical Monte Carlo Simulations”. In: *ACS Earth and Space Chemistry* 7.4 (2023), pp. 850–862.