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Julien Joliat, Théo Lenoir, Sylvain Picaud. Comparative Study of the Adsorption of 1- and 2-Propanol on Ice by Means of Grand Canonical Monte Carlo Simulations. ACS Earth and Space Chemistry, 2023, 7 (4), pp.850-862. 10.1021/acsearthspacechem.2c00390 . hal-04050061

**HAL Id: hal-04050061**

**<https://hal.science/hal-04050061>**

Submitted on 27 Apr 2023

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# A Comparative study of the Adsorption of 1- and 2-Propanol on Ice by Means of Grand Canonical Monte Carlo Simulations.

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## Abstract

In this paper, we use Grand Canonical Monte Carlo simulations to compare the adsorption characteristics of two propanol isomers (1- and 2-propanol) on crystalline ice, at the temperature of 227 K (i.e., typical of the Earth's troposphere), for which experimental data are available in the literature. The adsorption isotherms simulated for these two isomers show a very good agreement with the reported experimental data, giving thus confidence in the two interaction potential models used in the calculations. The results of the simulations thus nicely support the experimental conclusion that 2-propanol is preferentially adsorbed on ice with respect to 1-propanol, at least in the low pressure range where only a few molecules are trapped by the ice surface. The accuracy of the approach used, as tested here in tropospheric conditions, opens the way for its use in modeling studies also relevant to astrophysical context.

# Keywords

Ice, Propanol, Grand Canonical Monte Carlo, Simulations, Planetary Science

# 1 Introduction

Among the dozens of molecules and their isotopologues which have been detected in the Solar System or, farther, in the interstellar medium (ISM), a lot of them are relatively small organic species including aldehydes, alcohols, acids, amines and carboxamides, i.e., the main functional groups needed to participate in prebiotic (photo)chemistry.<sup>1,2</sup> This specific interest for organic molecules in the Universe is strongly related to the search of the origin of life, because it has been long thought that more complex biomolecules could have been formed from these chemical building blocks.<sup>3,4</sup> The corresponding chemistry is strongly suspected to be catalyzed by interstellar grains, at the surface of which adsorption and diffusion processes of the reactants may, for instance, decrease energetic chemical barriers and make possible (heterogeneous) reactions that would have been very unlikely in the gas phase.<sup>5</sup> Such heterogeneous processes have also been invoked to explain the extra-terrestrial formation of organic molecules in the Solar System, where Mars, Enceladus, Europa and Titan have been cited as likely places for life far from Earth.<sup>6</sup>

One of the common features of these various environments is the presence of solid water. Indeed, whereas the refractory core of the interstellar dust grains is made of silicates and carbonaceous materials, the most abundant component of the frozen grain mantles is water, which exhibits very likely an amorphous-like structure.<sup>7</sup> On the other hand, water and especially water crystalline ice have been detected on the Jovian and Saturn's satellites, where the ice-water interfaces may be ideal places to develop complex organic chemistry.<sup>6,8</sup>

Thus, both crystalline and amorphous ice surfaces are frequently the invoked candidates for catalyzing the extra-terrestrial chemistry which might lead to the formation of prebiotic species.<sup>9,10</sup> Indeed, ice surfaces can i) concentrate and maintain the reactants close together or orientate them such a way that they are in a favorable configuration for the subsequent reactions, ii) participate directly in these reactions by reducing the activation energy or iii) act as passive third body absorbing part of the excess energy released in the corresponding processes.<sup>7</sup> In any case, the role played by the ice surface depends on the trapping properties

of the reactants, especially their binding energy with the underlying water molecules.<sup>11</sup>

Thus for years, numerous experimental studies (see for instance the reviews by Hama and Watanabe<sup>12</sup> or Minissale et al.<sup>13</sup>) have been devoted to an accurate characterization of the interactions between organics and ice, which eventually appears crucial when considering interstellar heterochemistry.<sup>7</sup> Besides, the adsorption characteristics can also be described by means of computational approaches either based on quantum chemistry methods<sup>7</sup> or on the description of the intermolecular interactions by classical force fields.<sup>14</sup> Interestingly, it should be mentioned that these theoretical investigations may in certain situations, overcome some of the experimental limitations, for instance the accessible range of temperatures, or more simply, the corresponding cost of sophisticated instrumental devices.

However, the accuracy of any outcome of numerical simulation of adsorption processes depends on how the intermolecular interactions have been modeled. For instance, the results of quantum calculations performed in the DFT framework may vary when changing the functional or the size of the basis sets which have been selected. Similarly, the parametrization of classical force fields may impact on the transferability of the results from one situation to another one. It thus remains safer to compare the conclusions of various approaches, especially theoretical vs experimental ones (when possible), to validate the information obtained on molecular adsorption on ice.

Thus, in a series of previous studies,<sup>15-17</sup> we have compared the results obtained from grand canonical Monte Carlo (GCMC) simulations to those of the corresponding experimental investigations to estimate the accuracy of the force fields that can be used to model the interaction between small alcohol molecules and ice. Indeed, among other theoretical approaches, the GCMC method<sup>18,19</sup> has proven to be particularly suitable to give very useful and detailed information on the adsorption process of small organic compounds on ice, provided that the corresponding interactions are correctly modeled.<sup>15-17,20-37</sup>

Here, we complete these previous simulations by considering the adsorption behavior on ice of the two isomers of the propanol molecule (i.e., the 1- and 2-propanol molecules, for

which the OH group is bound either to a terminal or to the central carbon atom of the aliphatic chain, respectively) for which experimental results are available, coming however from two very different methods.<sup>38,39</sup> The interest for such investigation is twofold.

First, in the experiments, it has been inferred, from the comparison of the Langmuir constants (i.e., the ratio of the adsorption rate constant over the desorption rate constants), that the partitioning of the 2-propanol to the ice surface could be larger than that of 1-propanol. Because this difference could either come from the different location of the hydroxyl group in the alcohol molecules or, more simply, to the different experimental techniques that have been used to characterize their trapping on ice,<sup>39</sup> it certainly deserves additional investigations. We thus use here GCMC simulations performed in the same conditions as the experiments to shed light on the comparative behavior of these two propanol isomers at the surface of ice. Notice that it is the first time that this approach is devoted to the characterization of the influence of the isomerization on the adsorption properties on ice.

Secondly, in addition to this fundamental question, the results of such numerical investigations could be also somehow related to the very recent detection of both propanol isomers in the interstellar medium,<sup>40</sup> right after the presence of propanol has been suspected, for instance, in the comet 67P/Churyumov-Gerasimenko,<sup>41</sup> or at the surface of Enceladus.<sup>42</sup> Indeed, taking into account that chemical models indicate that both isomers of propanol are most likely produced within the dust-grain ice mantles,<sup>40</sup> the possible influence of the ice substrate on the detected abundance of these two isomers certainly cannot be disregarded.

The present GCMC simulations could thus help at understanding more precisely the mechanisms by which the propanol isomers are trapped or released by the ice substrate after their formation, provided these simulations are based on sufficiently accurate force fields. Thus, by comparing the results of the available experimental data (obtained at temperatures typical of the Earth's troposphere) to those coming from the simulations performed in similar conditions, we may assess the accuracy of the potential models used to describe the interaction between the propanol molecules and the ice surface, which likely opens the way

for possible use in other conditions, more typical of astrophysical environments.

The present paper is organized as follows. The details of the GCMC simulations are provided in Section 2 and the corresponding results are discussed in Section 3. The main conclusions of this study are finally summarized in section 4.

## 2 Methodology

The adsorption of propanol ( $\text{C}_3\text{H}_8\text{O}$ ), at the surface of  $\text{I}_h$  ice<sup>43</sup> has been investigated by means of GCMC simulations following the procedure recently used to simulate the adsorption of a series of alcohol molecules on ice,<sup>17</sup> at various temperatures characteristics of the Earth's troposphere and corresponding to those considered in the available experimental studies.<sup>38,39</sup> This procedure, which allows both the simulations of the adsorption isotherms and a thorough analysis of the adsorption characteristics, is only briefly recalled here.

All the simulations have been performed using the Monte Carlo general purpose GIBBS software package.<sup>44</sup> A simulation box of dimensions  $L_x = 35.926 \text{ \AA} \times L_y = 38.891 \text{ \AA} \times L_z = 100 \text{ \AA}$ , has been considered, in which an ice crystal containing 2880 water molecules, arranged in 18 layers, along the (0001) crystallographic direction (i.e., the  $z$  axis) has been introduced before the simulations start. The values of  $L_x$  and  $L_y$  have been chosen according to the periodicity of the ice crystal along the  $x$  and  $y$  axes whereas two gas/ice interfaces have been created in the simulation box by leaving empty a large space above and below the ice slab. Periodic boundary conditions have been applied along all the three axes of the simulation box ( $x$ ,  $y$  and  $z$ ) and the same simulation box has been used for all the temperatures considered here, taking into account that variations of the ice lattice parameters have been measured to be negligible in the corresponding small temperature range.<sup>45</sup>

For the simulations of the adsorption isotherms, a typical run has been started with an equilibration phase of  $2\text{--}6 \times 10^8$  Monte Carlo (MC) steps, depending on the chemical potential, followed by a production stage ranging from 1 to  $1.5 \times 10^8$  MC steps. In these

simulations, propanol molecules have been considered as being flexible, and thus, insertion, deletion, translation, rotation and configurational-biased regrowth (i.e., change of the internal molecular configuration) MC moves have been used, each of which being performed with the same probability of 20%.<sup>16</sup> Notice that for efficient insertion and partial regrowth moves, the Gibbs code uses the configurational-bias Monte Carlo technique associated with a reservoir of thermodynamically relevant trial internal molecular conformations generated beforehand.<sup>44,46</sup> In contrast to propanol, the water molecules of the ice substrate have been kept rigid and, thus, they have been only subject to rotation and translation moves, performed with equal trial probabilities.

In these GCMC simulations, the intermolecular interactions between propanol and water molecules have been described by classical force field models, consisting of a sum of the pairwise Lennard-Jones dispersion-repulsion and Coulomb electrostatic contributions of all pairs of interaction sites located on the  $C_3H_8O$  and  $H_2O$  molecules. In this approach, the water molecules have been described by the rigid TIP4P/ice model, which is well-suited to represent the solid-phase properties of water.<sup>47,48</sup>

The propanol molecules have been represented by the flexible AUA4 force field,<sup>49</sup> because it has been recently shown to give convincing results when used to characterize the adsorption of C2-C5 alcohols on ice under various conditions including the temperature of the Earth's troposphere and of the surface of Enceladus.<sup>16,17</sup> For comparison, we have also used the older OPLS-UA<sup>50</sup> interaction model to represent the propanol molecules. These two models (AUA4, OPLS-UA) are based on a simplified, united atom (UA) description of the propanol molecules, in which  $CH_x$  groups are treated as single interaction sites (i.e., they are considered as pseudoatoms located at the sites or near the sites of the carbon atoms), whereas all other atoms (e.g., hydroxyl O and H) are explicitly modeled. Note that using, at the expense of the numerical cost, an all-atom interaction potential instead of such united atom force fields has not proven to be more accurate in describing the overall properties of aqueous mixtures of propanol and water molecules in recent molecular dynamics simulations.<sup>51</sup>



Here, cross-interactions between water and propanol molecules have been calculated using the usual Lorentz-Berthelot combination rules for the determination of the LJ parameters.<sup>19</sup> The LJ contributions to the interaction potential have been truncated at a cutoff distance equal to half the smallest edge length of the simulation box, and long-range corrections have been used,<sup>46</sup> whereas the electrostatic interactions have been calculated by using the usual Ewald summation.<sup>19</sup>

In a GCMC simulation run, the chemical potential is fixed, allowing the number of molecules to fluctuate, at given temperature conditions. Thus, by varying the chemical potential, the number of molecules that are in contact with the ice surface can be calculated as a function of the chemical potential, which by definition corresponds to a simulated adsorption isotherm. However, for comparison with experimental data, it is more relevant to express the results of such simulations in terms of pressure instead of chemical potential. Taking into account that, instead of the chemical potential, the GIBBS code allows to work directly with the fugacity, a reliable conversion from fugacity to pressure thus needs to be achieved. Here, this has been based on a Widom procedure, as in our previous works,<sup>17,52</sup> which allows consistency with the interaction potential model used in the simulations.<sup>17,52</sup>

### 3 Results and discussion

Experimental data on the adsorption of 1-propanol molecules at the surface of ice  $I_h$  are available at 228 K,<sup>38</sup> whereas the corresponding experiments have been performed at 227 K for 2-propanol.<sup>39</sup> Here, the GCMC simulations have been carried out at 227 K for both 1- and 2-propanol molecules, knowing that the corresponding results at 228 K for 1-propanol are available in our previous study.<sup>17</sup> Let us first present in Fig. 1, the average number  $\langle N \rangle$  of alcohol molecules found in the basic simulation box as a function of the alcohol fugacity for both propanol isomers, as obtained using the AUA or the OPLS-UA force fields considered in the calculations. Notice that the corresponding curves can actually be viewed as adsorption

isotherms on ice, because the alcohol molecules are almost never found dissolved into the bulk ice phase nor isolated in the vapor phase above the ice surface in the GCMC simulations (i.e.,  $\langle N \rangle$  represents in fact the number of adsorbed molecules).

All the simulated isotherms (Fig. 1) exhibit a rapid increase of  $\langle N \rangle$  at low fugacity values, corresponding to the building up of the adsorption layer. Then, in a broad range of values, the change of the fugacity results only in a small variation of  $\langle N \rangle$ , which is a strong indication of the formation of a stable monolayer at the ice surface for each of the two propanol isomers. Finally, the 3-dimensional condensation of the alcohol molecules at the surface of ice is evidenced by the sudden jump of the isotherms at the threshold value  $f_0$  of the fugacity. It can also be seen on Fig. 1a that the simulated adsorption isotherms at 227 and 228 K<sup>17</sup> for 1-propanol are almost superimposed, indicating the weak effect of such a small temperature change on the GCMC results.

Then, the adsorption behavior of the propanol molecules at the surface of ice has been more precisely investigated by selecting two values of the fugacity, which illustrate two different typical situations (see Fig. 1). At the low fugacity value defining System 1, only very few molecules are adsorbed at the surface, whereas at the higher fugacity value corresponding to System 2, the propanol molecules form an almost saturated layer on ice, just below the point of condensation. For each situation, configurations have been saved every  $2 \times 10^4$  steps during the production phase of the GCMC runs, thus providing a set of  $5-7.5 \times 10^3$  sample configurations (for Systems 2 and 1, respectively) that have been used for a detailed statistical analysis of the adsorbed phase. Note that the number of sample configurations has been chosen to be larger for System 1 than for System 2, for better statistics because of the weak number of adsorbed molecules in System 1.

The number density profiles calculated at 227 K along the  $z$  axis of the simulation box for the two propanol isomers and the two force fields considered here are shown in Fig. 2, together with the upper part of the number density profile for the water molecules of the ice phase, for reference. In calculating these profiles, the position of a given molecule has been

represented by that of its center of mass. Moreover, for the propanol molecules, the profiles shown have been averaged over the two interfaces present in the basic box, to improve the statistics.

First, it clearly appears that the two potential models used here for describing the propanol molecules lead to very similar results. Thus, as shown in Fig. 2, the number density profile  $\rho_{\text{CM}}(z)$  calculated for System 1 exhibits only one very small peak, located near the ice surface, for all the situations considered here. This shows that, at the corresponding value of the fugacity, only very few molecules are trapped at the ice surface. In addition, the peaks corresponding to 1- and 2-propanol are slightly shifted relative to each other by about 0.5 Å, indicating that the centers of mass of the 1-propanol molecules are, in average, located slightly farther from the surface than those of the 2-propanol molecules. This could come not only from the different internal geometry of the propanol isomers, but also from their possible different orientations in the corresponding adsorption sites. For System 2, a similar behavior is obtained, however with a much larger intensity of the single peak observed in  $\rho_{\text{CM}}(z)$ , corresponding to a larger number of molecules adsorbed at the ice surface in this situation. This feature, combined with a careful analysis of snapshots taken from the simulations (as shown in the insets given in Fig. 2), indicates that the propanol molecules form a single monolayer at the surface, at this value of the fugacity just before 3D condensation occurs. In addition, the analyses of the condensed phase at larger fugacity values (not shown) confirm that this monolayer is almost saturated, as previously evidenced for 1-propanol adsorption on ice at 228 K.<sup>17</sup> Note that the single peak in  $\rho_{\text{CM}}(z)$  also slightly shifts to larger  $z$  values when the fugacity increases, suggesting a modification of the propanol orientations upon coverage increase.

The analysis of the molecular orientations at the surface of ice has been carried out as previously,<sup>17</sup> i.e., by using three different angles. The first one,  $\theta_1$ , defines the orientation of the molecular axis, with respect to the vector  $z$  normal to the gas/ice interface, pointing from the ice to the gas phase. Note that the molecular axis points from the C atom of the

terminal aliphatic group ( $\text{CH}_3$ ) to the C atom which is bounded to the alcoholic function in the case of the 1-propanol molecule, whereas it points from one methylic carbon ( $\text{CH}_3$ ) to the other one, for the 2-propanol isomer. Thus, while a value of  $\theta_1 = 0$  corresponds to an orientation of the molecular axis perpendicular to the ice surface for both isomers, in this situation the C-O bond points up to the gas phase in the case of the 1-propanol, whereas it lies parallel to the ice surface, in the case of the 2-propanol.

The two other angles,  $\theta_2$  and  $\theta_3$ , give the orientation of the CO vector, pointing from the alcoholic C to the O atom ( $\theta_2$ ), and of the OH vector, pointing from the O to the H atom of the hydroxylic group ( $\theta_3$ ), with respect to  $z$ . The values  $\theta_2 = 0$  and  $\theta_3 = 0$  correspond to configurations where the CO and OH vectors are oriented perpendicular to the ice surface.

The orientational distributions are given in Fig. 3 and Fig. 4, for the 1- and 2-propanol isomers, respectively, and for the two interaction models considered here. In these figures, the geometry of the two propanol isomers and the definition of the three angles are given as insets, for clarity.

Overall, the choice of the potential model does not strongly influence the results obtained, indicating that the orientations of the propanol molecules on ice does not depend too much on the united atom model which is used in the simulations.

For the angle  $\theta_1$ , the two propanol isomers exhibit different behaviors, which can of course be partly related to the different internal geometry of these molecules. Thus, for 1-propanol (Fig. 3), the distribution obtained at the very low surface coverage corresponding to System 1, is characterized by a single, rather broad, peak, the maximum of which being around the value  $\cos\theta_1$  equal to  $-0.5$ . Taking into account the rather large full width at half maximum (FWHM) of this peak, we can conclude that the orientations of the 1-propanol molecules correspond to values of the angle  $\theta_1$  that are in the range of  $[105-135]^\circ$ . They are thus related to tilted orientations of the C-C axis in the adsorption sites, i.e., a situation in which the methyl group is located farther from the ice surface than the OH group. In the case of the 2-propanol molecules (Fig. 4), the  $P(\cos\theta_1)$  distribution exhibits a single, broad peak,

the maximum of which being around the value  $\cos\theta_1$  equal to 0, with a full width at half maximum (FWHM) equal to about 0.5. This indicates that the orientations of the C–C axis range between  $75$  and  $105^\circ$ , values that correspond to tilted orientations in which the OH group points down to the ice surface, when considering System 1.

Upon increasing the coverage up to the monolayer completion (System 2), the two propanol isomers clearly reorient at the ice surface, as shown by the splitting in two peaks of the  $P(\cos\theta_1)$  distributions (Fig. 3 and Fig. 4). For the 1-propanol molecules, the main peak of the distribution indicates that this reorientation can lower the molecular axis down to an angle value of about  $\theta_1 = 155^\circ$ . In this configuration, the polar head of the 1-propanol molecule still points down to the ice surface. In addition, the large broadening of the smaller peak of this  $P(\cos\theta_1)$  distribution up to positive values indicates that other configurations of the molecules are also allowed at the ice surface, including those where the molecular axis lie more or less parallel to the surface ( $\cos\theta_1 = 0$ ). In the case of the 2-propanol molecules, the two, rather broad peaks obtained in the  $P(\cos\theta_1)$  distribution correspond to angular values equal to about  $\theta_1 = 55^\circ$  and  $\theta_1 = 125^\circ$ , which both denote configurations in which the C–O bonds point toward the ice surface. Note however that in the above mentioned situations, the exact orientation of the polar head of the alcohol molecule, especially the orientation of the OH vector, cannot be unambiguously determined without a careful, combined analysis of the two other angular distributions.

In contrast to  $P(\cos\theta_1)$ , the angular distributions corresponding to angles  $\theta_2$  and  $\theta_3$  exhibit similar behavior for the two propanol isomers, which indicates similar orientations of their polar heads at the ice surface. Thus, for both isomers,  $P(\cos\theta_2)$  is characterized by a single peak around the value  $-0.8$  for System 1, corresponding to an orientation of the CO vector that points rather toward the water molecules when the adsorbed molecules are nearly isolated on the ice surface. This peak shifts to  $\cos\theta_2$  value of about  $-0.5$  when increasing the fugacity value from System 1 to System 2, a feature which can be related to a reorientation of the CO vector, which thus tends to lie more parallel to the ice surface at higher coverage

corresponding to the completion of one monolayer. Meanwhile, the split of the peak observed in  $P(\cos\theta_3)$  upon increasing coverage indicates that this CO reorientation is concomitantly accompanied by a change of the orientation of the OH vector, with three preferred values for the  $\theta_3$  angle corresponding to about 75, 125, and 155°. Taking into account that the propanol molecules are flexible in the GCMC simulations, all the above mentioned features can be related to the formation of proton donor and proton acceptor hydrogens bonds between the alcohol molecules and the surface water molecules and, as the coverage increases, also between the neighboring alcohol molecules themselves. Such a behavior has already been observed for other alcohols molecules interacting with the ice surface.<sup>17</sup> Note that the internal conformation of the adsorbed propanol molecules has also been characterized by the analysis of the distributions of the torsional angles which involve the OH group. The corresponding results (not shown) are very similar for the two potential used in the simulations and does not evidence any significant torsions of the molecules upon adsorption and coverage increase.

Finally, the adsorption process can also be characterized from an energetic point of view. Considering that the total energy of an adsorbed molecule comes from its interaction with the ice surface as well as with the other adsorbed molecules, we have calculated separately the distributions of the energy between one adsorbed propanol molecule and the water molecules ( $U_{ads-w}$ ), and between this alcohol molecule and the other adsorbed propanols ( $U_{ads-ads}$ ), for the two values of the fugacity corresponding to Systems 1 and 2.

As it can be seen on Fig. 5, the overall behavior of these energy distributions appears very similar for both propanol isomers, especially when considering System 1, irrespective of the interaction potential model. Thus, for System 1, the  $P(U_{ads-w})$  distribution exhibits a single, rather broad, peak, corresponding to a mean value of  $U_{ads-w}$  equal to  $-67.3 \pm 10.1$  and  $-72.7 \pm 12.7$  kJ.mol<sup>-1</sup> for the 1-propanol, and to  $-69.2 \pm 10.8$  and  $-73.7 \pm 10.2$  kJ.mol<sup>-1</sup> for the 2-propanol, when using the AUA and the OPLS-UA models, respectively. These values indicate that the two propanol isomers typically form three hydrogen bonds with the water molecules at low coverage of the ice surface, as already shown for other small alcohol

molecules interacting with ice.<sup>17</sup> Meanwhile, the corresponding  $P(U_{ads-ads})$  distributions are also characterized by a single peak, located near zero, indicating that most of the propanol molecules can be considered as being nearly isolated from each other on the ice surface. As a consequence,  $U_{ads-w}$  certainly gives a good estimate of the adsorption energy at low propanol coverage of the ice surface. It should be however noted that the extension of the peak in  $P(U_{ads-ads})$  towards lower energy values (typically down to  $-15 \text{ kJ.mol}^{-1}$ ) also shows the existence of a residual interaction between the propanol molecules. This can be related to the fact that we have chosen to define System 1, a fugacity value corresponding to a surface coverage which cannot be rigorously vanishingly small, for statistical reasons. Anyway, the small energy differences which are calculated between the two propanol isomers, with slightly lower values of  $U_{ads-w}$  for 2-propanol than for 1-propanol, could indicate a preferred adsorption of the former isomer with respect to the latter one, at least at the very low pressure values corresponding to System 1. Although these differences, which remains less than  $2.0 \text{ kJ.mol}^{-1}$ , irrespective of the model used in the simulations, are likely not much larger than the expected accuracy of such interaction potential models, it has to be mentioned that the value of the mean energy  $U_{ads-w}$  nicely agrees with the experimental estimation of the adsorption energy for 1-propanol on ice ( $-68.2 \text{ kJ.mol}^{-1}$ ).<sup>38</sup> Unfortunately, we are not aware of any corresponding value for the 2-propanol.

When considering the larger value of the fugacity corresponding to the completion of one propanol layer at the surface of ice (i.e., System 2), the two propanol isomers still exhibit similar behavior, although the values of their lateral interaction energy  $U_{ads-ads}$  are not exactly the same. Indeed, while the peak in  $P(U_{ads-w})$  shifts toward higher energy value, typically around  $-40 \text{ kJ.mol}^{-1}$ , for both 1- and 2-propanol molecules, the peak in  $P(U_{ads-ads})$  not only shifts toward lower values, but also splits into one major and one minor peaks. In this  $P(U_{ads-ads})$  distribution, a difference of about  $5 \text{ kJ.mol}^{-1}$  is obtained between 1- and 2-propanol, the two peaks corresponding to energy values of about  $-50$  and  $-25 \text{ kJ.mol}^{-1}$ , and  $-45$  and  $-20 \text{ kJ.mol}^{-1}$  for 1- and 2-propanol, respectively. Nevertheless,

these two peaks can be attributed to the formation of 1 or 2 more or less strong hydrogen bonds between neighboring adsorbed molecules.

Overall, the energetical analysis evidences a large increase of the lateral interactions between the propanol molecules at the expense of their interaction with ice, upon increasing the coverage. This can be related to the conclusions of the orientational analysis, which shows different orientations of the molecular axes of the two propanol isomers at high coverage (leading thus to slightly different lateral interaction energies  $U_{ads-ads}$ ), while the orientation of their hydroxyl group with respect to the ice surface remains similar (resulting thus in similar  $U_{ads-w}$  values).

## 4 Comparison with experimental data

Experimental measurements of the adsorption isotherms of 1-propanol on ice have been obtained by means of coated wall flow tube experiments performed at 228 K.<sup>38</sup> These experimental results are thus compared in Fig. 6a to those obtained here by means of GCMC simulations performed at 227 K, using both AUA and OPLS-UA interaction potential models. In this figure, the adsorption isotherms are shown on the form of the 1-propanol uptake ( $\Gamma$ ) expressed in  $\mu\text{mol}/\text{m}^2$ , as a function of the pressure (in Pa). Overall, these isotherms exhibit very similar shape, as already obtained in our previous study where the GCMC simulations were performed at 228 K, with however, the AUA potential model, only.<sup>17</sup> As also noticed previously,<sup>17</sup> the results given in Fig. 6a evidence a small temperature shift between the simulated and measured isotherms, and the results of additional simulations performed at slightly higher temperature, typically 233 K (blue curves), exhibit an even better agreement with the experimental data, on a large pressure range and for the two interaction potential models used in the present simulations.<sup>17</sup> Notice however that, at higher pressures, the agreement is a little bit less satisfactory, although the rather large scattering of the experimental data should be pointed out.



In the case of the 2-propanol isomer, experimental data have been obtained at 227 K, by means of X-ray photoelectron spectroscopy and converted as isotherms in the form of the coverage expressed as fractions of monolayer (ML) as a function of the alcohol pressure.<sup>39</sup> In this experimental study, the coverage has been defined as the measured number of adsorbed molecules at the surface, divided by the saturated surface coverage  $\sigma_{sat}$  as calculated from a Langmuir analysis of the experimental data. In addition, Newberg and Bluhm<sup>39</sup> also converted on the same way (i.e., coverage (ML) as a function of the alcohol pressure) the experimental results obtained on 1-propanol by Sokolov and Abbatt,<sup>38</sup> for comparison.

Thus, to compare the isotherms simulated in the present work with those experimentally obtained for both propanol isomers,<sup>39</sup> we have performed a Langmuir analysis of the results of the simulations, and calculated the corresponding simulated  $\sigma_{sat}^{sim}$  values for both propanol isomers, which have then been used to define the coverage values issued from our theoretical approach. This Langmuir analysis has been performed from the results obtained using both AUA and OPLS-UA potential models, as previously described.<sup>17</sup> However, it is important to note that the behavior of both propanol isomers on ice can be well represented by the Langmuir isotherm (not shown) only in a pressure range for which the lateral interactions between the adsorbed molecules remain weak, as already observed for a series of small alcohol molecules.<sup>17</sup> As a consequence, the values of  $\sigma_{sat}^{sim}$  are slightly smaller than the actual simulated coverages at saturation, which can be roughly estimated by the number  $N_{max}$  of adsorbed alcohol molecules in System 2, as shown in Fig. 1 (see Table 1 for these values). However, because the experiments have also been performed in a relatively low pressure range, only, and their results have been extrapolated from such a Langmuir analysis, it appears more suitable to use  $\sigma_{sat}^{sim}$  rather than  $N_{max}$  to calculate the simulated coverage values, that have to be used for the present comparison between theoretical and experimental results.

The experimental and theoretical values of the surface coverage as a function of the pressure are reported on Fig. 6b and Fig. 6c, for 1- and 2-propanol, respectively, the experimental

results being recorded from the original publications using WebPlotDigitizer.<sup>53</sup> On these figures, results of simulations performed at both 227 and 233 K have been plotted for the two propanol isomers, according to the above mentioned conclusion on the small temperature shift obtained when comparing experimental and simulated results for 1-propanol. Overall, all the isotherms given in Fig. 6 exhibit similar shape, although some subtle differences can be observed. Indeed, while the experimental isotherm (empty circles) for 1-propanol is perfectly well reproduced by the results of the simulations performed at 233 K (blue curves), irrespective of the potential model used (Fig. 6b), it appears that, for the 2-propanol isomer (Fig. 6c), the best agreement with the experiments is rather obtained when considering the simulated results at 227 K when the AUA potential model is used (pink crosses), and at 233 K when the calculations are performed with the OPLS-UA model (blue diamonds). These conclusions are similarly reflected by the numerical results of the Langmuir fits, given in Table 1. Indeed, the experimental values of the Langmuir parameters ( $\sigma_{sat}$  and  $K$ ) are well reproduced by both interaction potentials at 233 K for the 1-propanol isomer, while when considering the 2-propanol, the AUA model appears to work better at 227 K, and the OPLS-UA one at 233 K. These features seem to indicate that each force field parametrization has a different temperature scale, at least when considering the 2-propanol species. Anyway, taking into account the present results and the usual precision of parametrized classical force fields, it is safer to conclude that the two potential models used in the present simulations are accurate enough to give a correct characterization of the adsorption of the two propanol isomers on ice, with a shift not larger than 5 K with respect to the experimental results.

In addition, in the analysis of the experimental results made by Newberg and Bluhm,<sup>39</sup> it has been suggested that the partitioning to ice of 2-propanol may be greater than that of 1-propanol, because the isotherm for the former molecule is characterized by slightly larger coverage values than for the latter one, on the whole investigated pressure range. As a consequence, it has also been stated that the 2-propanol molecule appears to bind more strongly to ice than the 1-propanol.<sup>39</sup> However, these conclusions have been cautiously drawn

because the corresponding experiments have been done using very different techniques and, as a consequence, their comparison might be not quantitative.

Following a similar approach, the isotherms for the two propanol isomers adsorbed on ice at the same temperature (227 and 233 K), as simulated by using either the AUA or the OPLS-UA potential models, are given in Fig. 7, for comparison. As it can be seen, at 227 K with the AUA model, the coverage values calculated for the 2-propanol are slightly larger than those obtained for the 1-propanol, at pressure values typically less than  $10^{-2}$  Pa. The reverse situation is evidenced at higher pressures, up to the saturation of one adsorbed monolayer on the ice surface. By contrast, when using the OPLS-UA potential model, at the same temperature of 227 K, the coverage values for 2-propanol are always larger than for 1-propanol, on the whole investigated pressure range up to the saturation. Very similar features are evidenced at 233 K, suggesting that, in the low pressure range considered in the experiments, 2-propanol actually adsorbed slightly better on ice than 1-propanol. This conclusion remains valid at higher pressures when using the OPLS-UA potential model in the simulations.

## 5 Conclusions

Here, the trapping of 1- and 2-propanol isomers on crystalline ice has been characterized by using GCMC simulations, performed with the AUA and OPLS-UA interaction potential models, in conditions for which experimental adsorption isotherms are available in the literature.<sup>38,39</sup> The simulated isotherms turned out to be in very good agreement with the experimental measurements for both molecules and interaction potential models, provided that a small temperature shift no larger than 5 K, between simulations and experiments is possibly taken into account, as previously concluded for a series of alcohol molecules.<sup>17</sup> Moreover, for the 1-propanol molecule, the adsorption energy calculated at low coverage of the ice surface, also nicely agree with the experimental value.<sup>38</sup> The results of the simula-

tions as obtained with both AUA and OPLS-UA interaction potential models nicely support the experimental findings that 2-propanol is preferentially adsorbed on ice with respect to 1-propanol, at least in the pressure range corresponding to low ice surface coverage, where this conclusion does not depend on the potential model used in the calculations. They also confirm that the internal geometry of the molecules can influence their interaction with ice and, thus, lead to different adsorption characteristics between different isomers of the same molecular species. In continuation of our previous works devoted to a large set of volatile organic compounds,<sup>14</sup> the results of the present simulations at the molecular scale shed light on the details of the adsorption mechanisms at the ice surface of two common industrial effluents. Together with the available experimental information, they thus may help at a better quantification of the influence of the heterogeneous chemistry in the Earth's troposphere and boundary layer, where the interaction of organic materials with environmental ices is thought to play an important role in a number of biogeochemical and climate processes.<sup>54</sup>

It is worth noting that the accuracy of both AUA and OPLS-UA models, as tested here in tropospheric conditions, opens the way for its use in modeling studies also relevant to an astrophysical context where molecular concentrations are usually low, and for which experimental measurements are, at present, very scarce. Although any quantitative comparison between the present results and these experimental data obtained under ultra high vacuum, at very low temperatures relevant for astrophysical environments, on both crystalline and amorphous ice surfaces,<sup>55,56</sup> should be very cautiously made without having explicitly performed the calculations in similar conditions, we can note that all these investigations evidence the strong ability of propanol molecules to hydrogen bond to the water molecules at the ice surface. In addition, it could be mentioned that, in the recent detection of propanol isomers in the ISM, 2-propanol was found to be slightly less abundant than 1-propanol, with an abundance ratio of 0.6,<sup>40</sup> whereas quantum calculations indicate that, from a strict energetic point of view, 2-propanol should have a larger abundance than 1-propanol, because it is more stable by about  $17 \text{ kJ.mol}^{-1}$ .<sup>57</sup> Such an apparent discrepancy could be, at least partly

related to the preferential adsorption of the 2-propanol molecule on ice, as obtained in the present simulations (in accordance with the experimental data) which thus might lead to a partial depletion of the 2-propanol concentrations in a gas phase interacting with ice surfaces or, reversly, to a preferential release of the 1-propanol with respect to the 2-propanol when these molecules are formed in the ice mantles of dust grains. Of course, this conclusion should be supported by additional calculations and experiments, considering also other solid forms of water such as amorphous ices, in temperature ranges typical of interstellar environments.

## **6 Acknowledgments**

This project is supported by the Region Bourgogne Franche-Comté through the grant PASCOA 2020-0052. Computations have been performed using resources of the Mésocentre de calcul de Franche-Comté.

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## Figures and tables

Table 1: Parameters of the best Langmuir fit to the simulated isotherms, for the two propanol isomers considered here, at 227 and 233 K. The simulated isotherms have been obtained using two different interaction potential models (AUA and OPLS-UA). Note that these isotherms exhibit a Langmuir behavior in the low pressure range, only. The simulated coverage  $N_{\max}$  at the saturation pressure is also given in parantheses, for information. Available experimental data for 1-propanol at 228 K,<sup>38</sup> and for 2-propanol at 227 K,<sup>39</sup> are also reported.

Temperature	Model	Molecule	$\sigma_{sat}^{sim} (N_{\max}) [10^{14} \text{ molecule.cm}^{-2}]$	$K [10^3 \text{ Torr}^{-1}]$
227 K	AUA	1-propanol	4.1 (4.3)	8.6
		2-propanol	3.6 (3.7)	5.7
	OPLS-UA	1-propanol	4.2 (4.5)	9.7
		2-propanol	3.7 (3.9)	10.4
233 K	AUA	1-propanol	4.2 (4.6)	3.1
		2-propanol	3.5 (3.8)	2.1
	OPLS-UA	1-propanol	4.2 (4.3)	4.1
		2-propanol	3.7 (3.9)	5.1
Exp. 228 K <sup>38</sup>		1-propanol	3.1	3.5
Exp. 227 K <sup>39</sup>		2-propanol	-	6.3

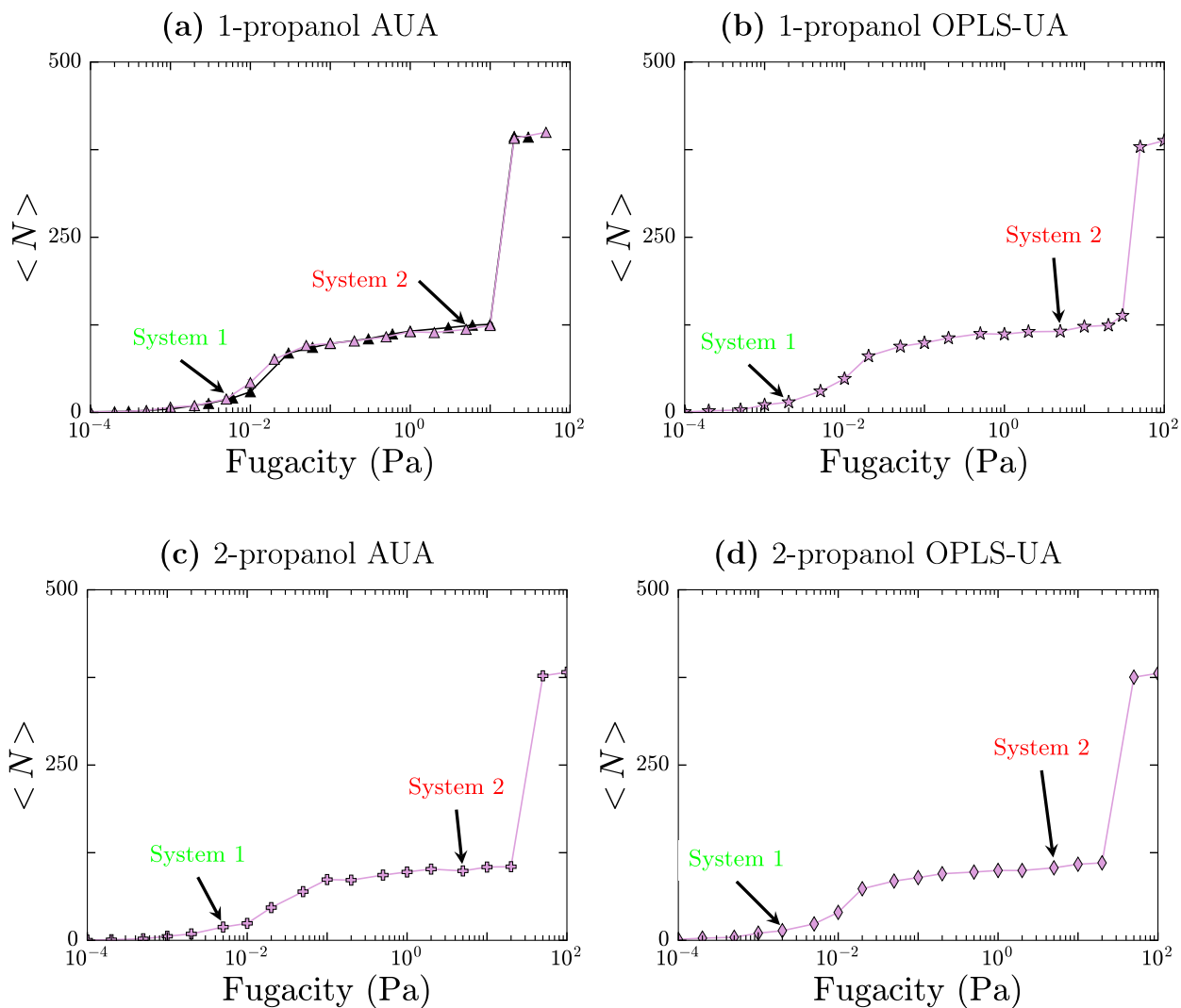


Figure 1: Average number of 1- and 2-propanol molecules in the basic simulation box as a function of the fugacity (note that the errors bars are smaller than the symbols), as calculated from the present GCMC simulations at 227 K (pink symbols and lines). The arrows indicate the systems used in the detailed analyses. Lines are only guide to the eye. Results are given using two different interaction models (AUA and OPLS-UA on the left and right hand sides of the figure, respectively). Additional results are also given for 1-propanol molecules, using the AUA model, at 228 K (black line and triangles).<sup>17</sup>

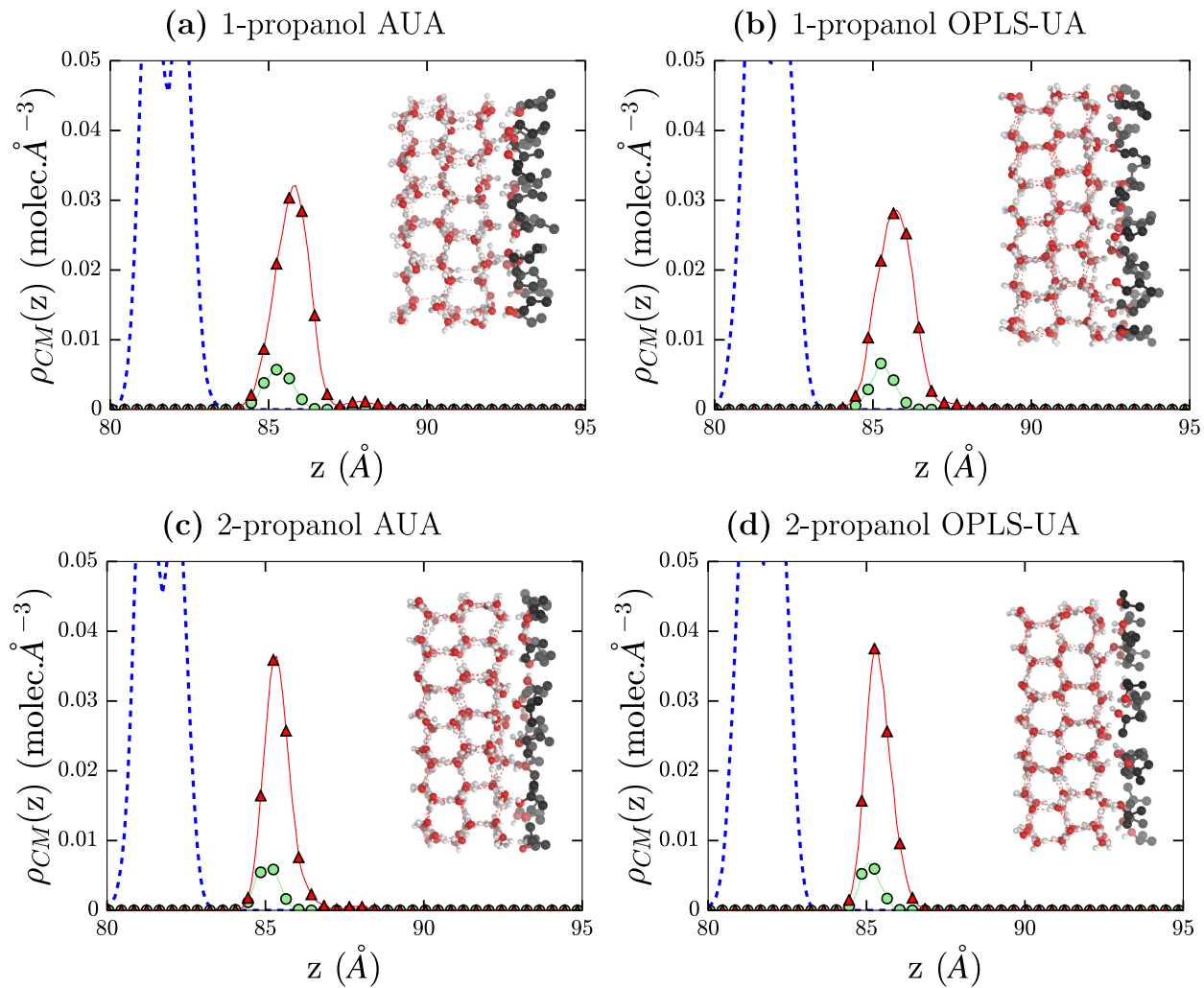


Figure 2: Number density profiles for 1- and 2-propanol centers of mass, in Systems 1 (green circles) and 2 (red triangles), as obtained from the simulations at 227 K. Results are given using two different interaction models (AUA and OPLS-UA on the left and right hand sides of the figure, respectively). For reference, the outer tail of the number density profile of the water centers of mass in System 1 is also given (dashed blue line). Note that this outer tail corresponds in fact to the surface water layer, only. In addition, snapshots issued from the simulations of System 2 are given, to illustrate the adsorption geometry when the propanol molecules form a nearly saturated monolayer at the ice surface. In these snapshots, the three outermost ice layers are shown. Oxygen, hydrogen and carbon (bottom carbon) atoms are represented as red, white, and black (gray) circles, respectively. Note that hydrogen atoms of the aliphatic chains are not shown because they are not explicitly included in the united atom potential models used in the simulations.

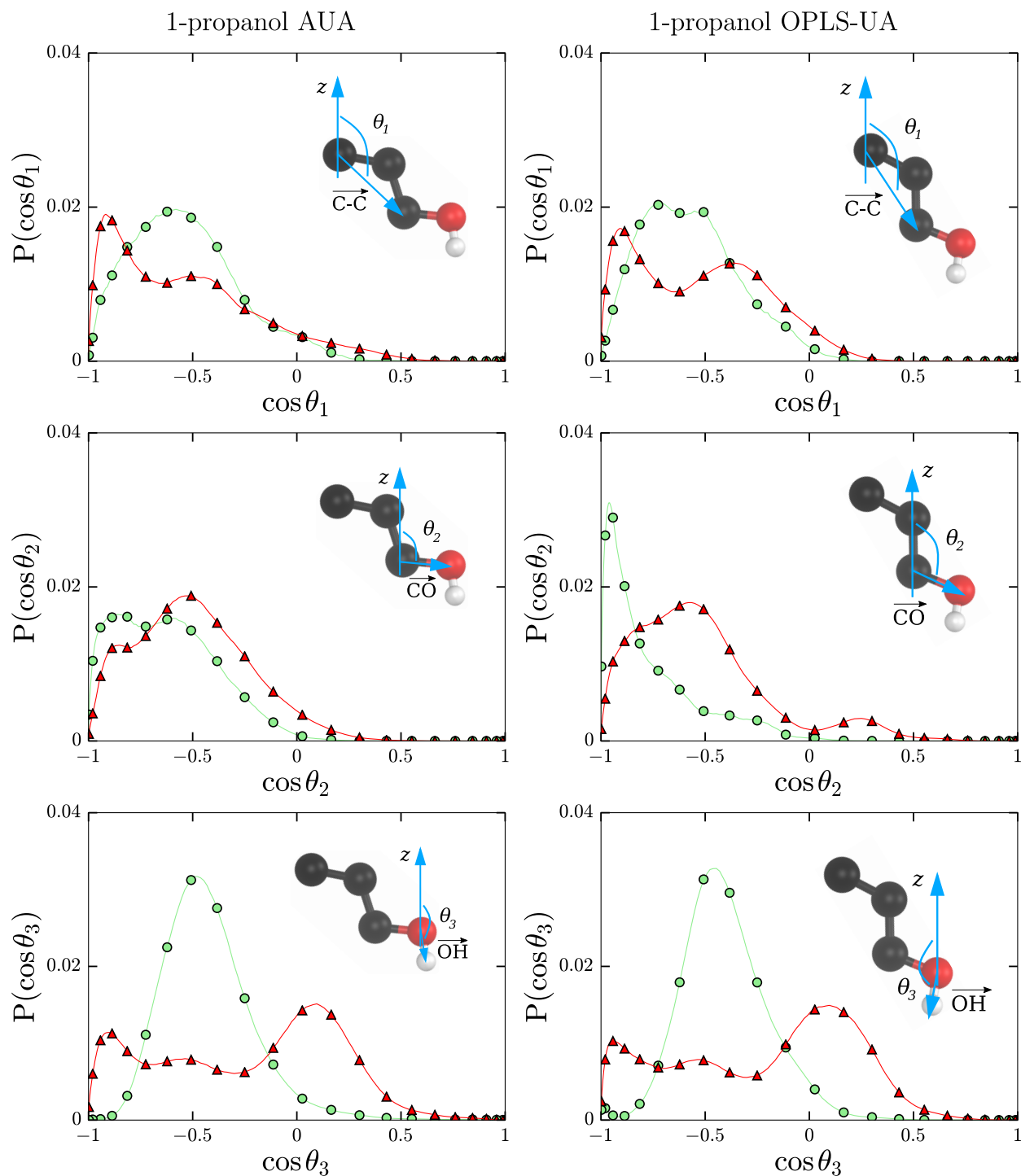


Figure 3: Distributions of the molecular orientations for the 1-propanol molecules adsorbed on ice, for Systems 1 (green circles) and 2 (red triangles), as obtained with the AUA (left) and the OPLS-UA (right) interaction potential models. Top row:  $\theta_1$  is the angle formed between the C-C vector and surface normal vector ( $z$ ); middle row:  $\theta_2$  is the angle formed between the CO vector and  $z$ ; bottom row:  $\theta_3$  is the angle formed between the OH vector and  $z$ . Inserts show the definition of the various angles considered.



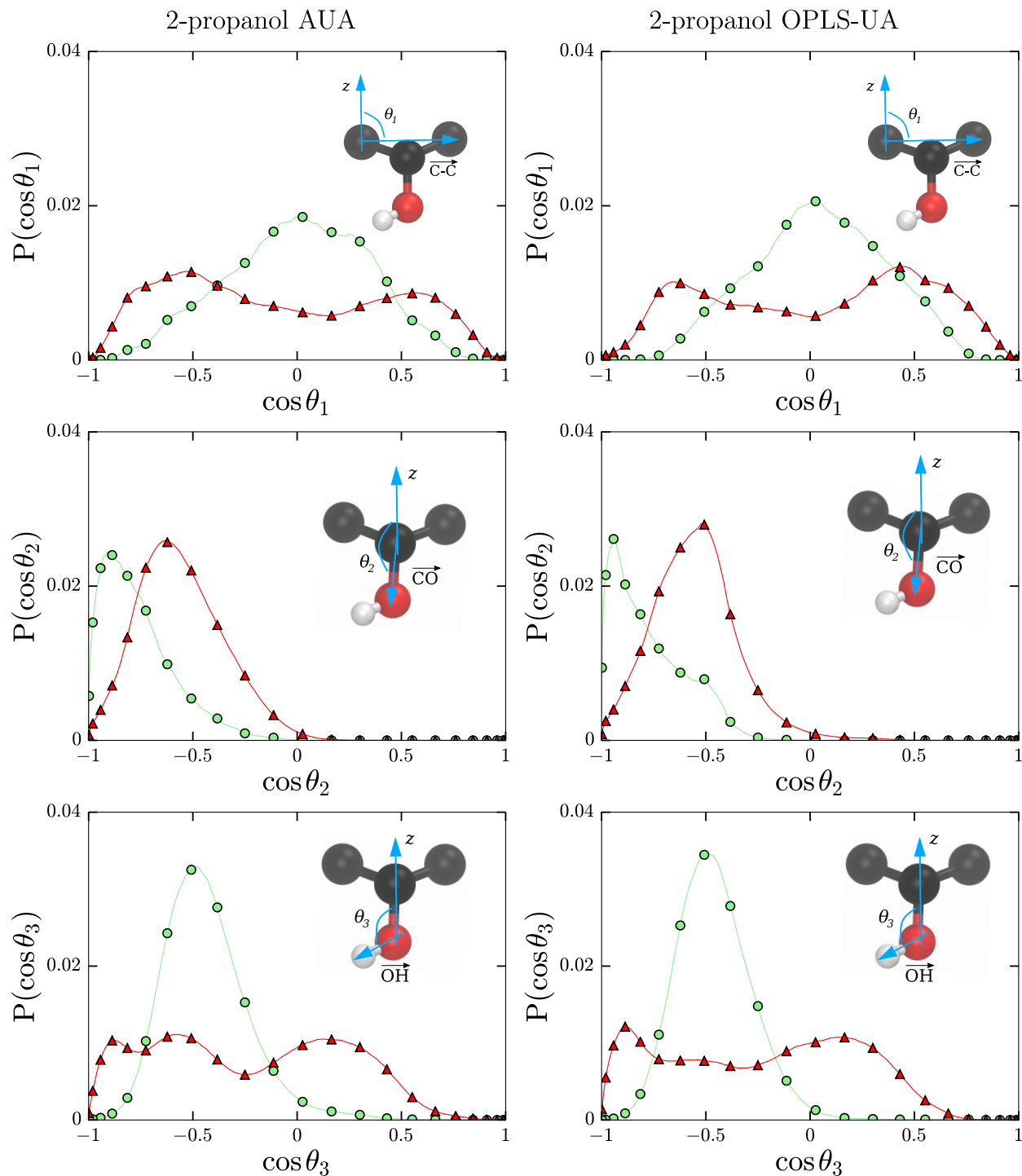


Figure 4: Distributions of the molecular orientations for the 2-propanol molecules adsorbed on ice, for Systems 1 (green circles) and 2 (red triangles), as obtained with the AUA (left) and the OPLS-UA (right) interaction potential models. Top row:  $\theta_1$  is the angle formed between the C-C vector and surface normal vector ( $z$ ); middle row:  $\theta_2$  is the angle formed between the CO vector and  $z$ ; bottom row:  $\theta_3$  is the angle formed between the OH vector and  $z$ . Inserts show the definition of the various angles considered.

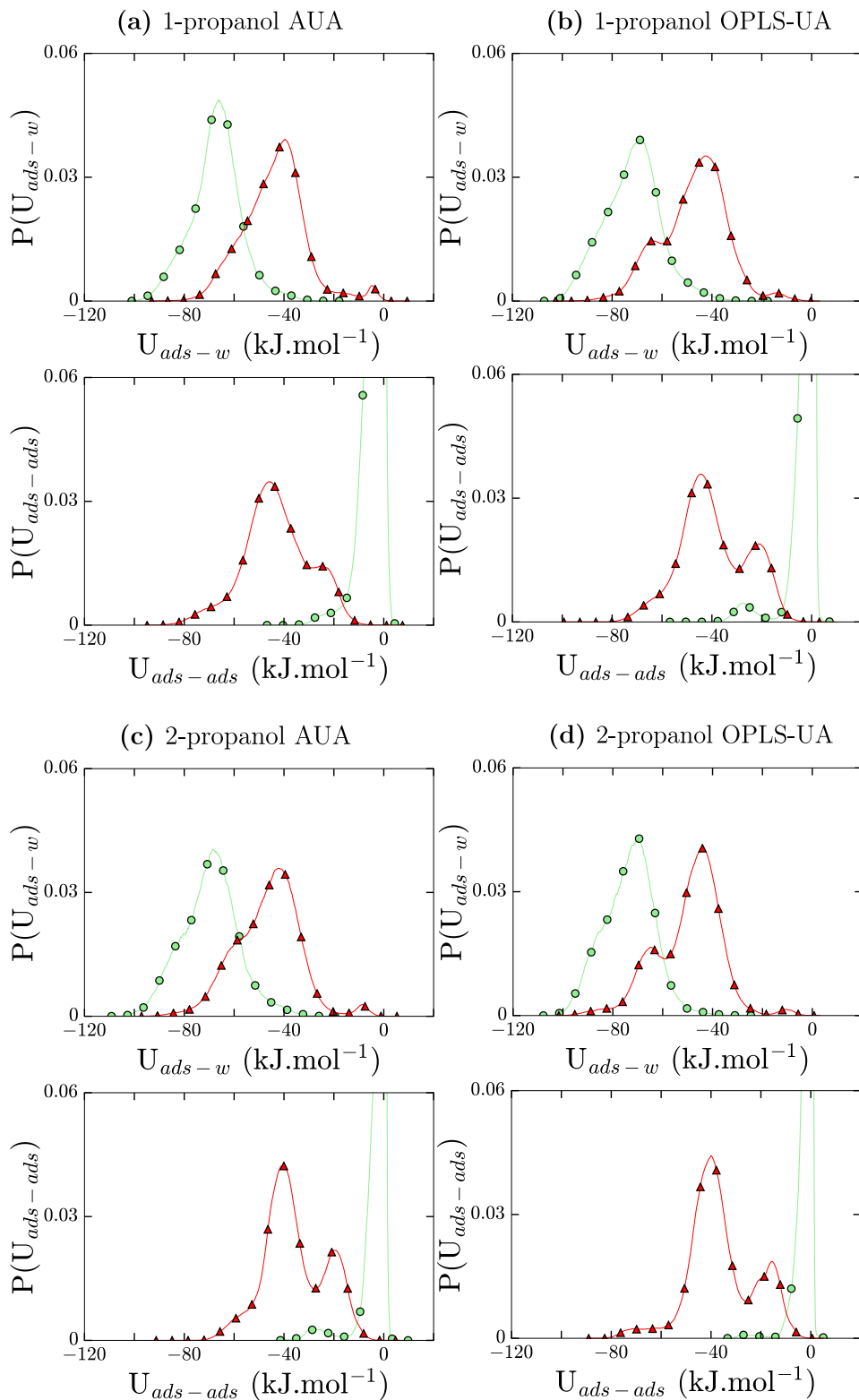


Figure 5: Distributions of the interaction energy of an adsorbed 1-propanol ((a) and (b)), or 2-propanol ((c) and (d)) molecule with the ice phase  $P(U_{ads-w})$  and with the other adsorbed propanol molecules  $P(U_{ads-ads})$  for Systems 1 (green circles) and 2 (red triangles), as calculated from the GCMC simulation results performed using either the AUA (left hand side of the figure) or the OPLS-UA (right hand side of the figure) interaction potential model.

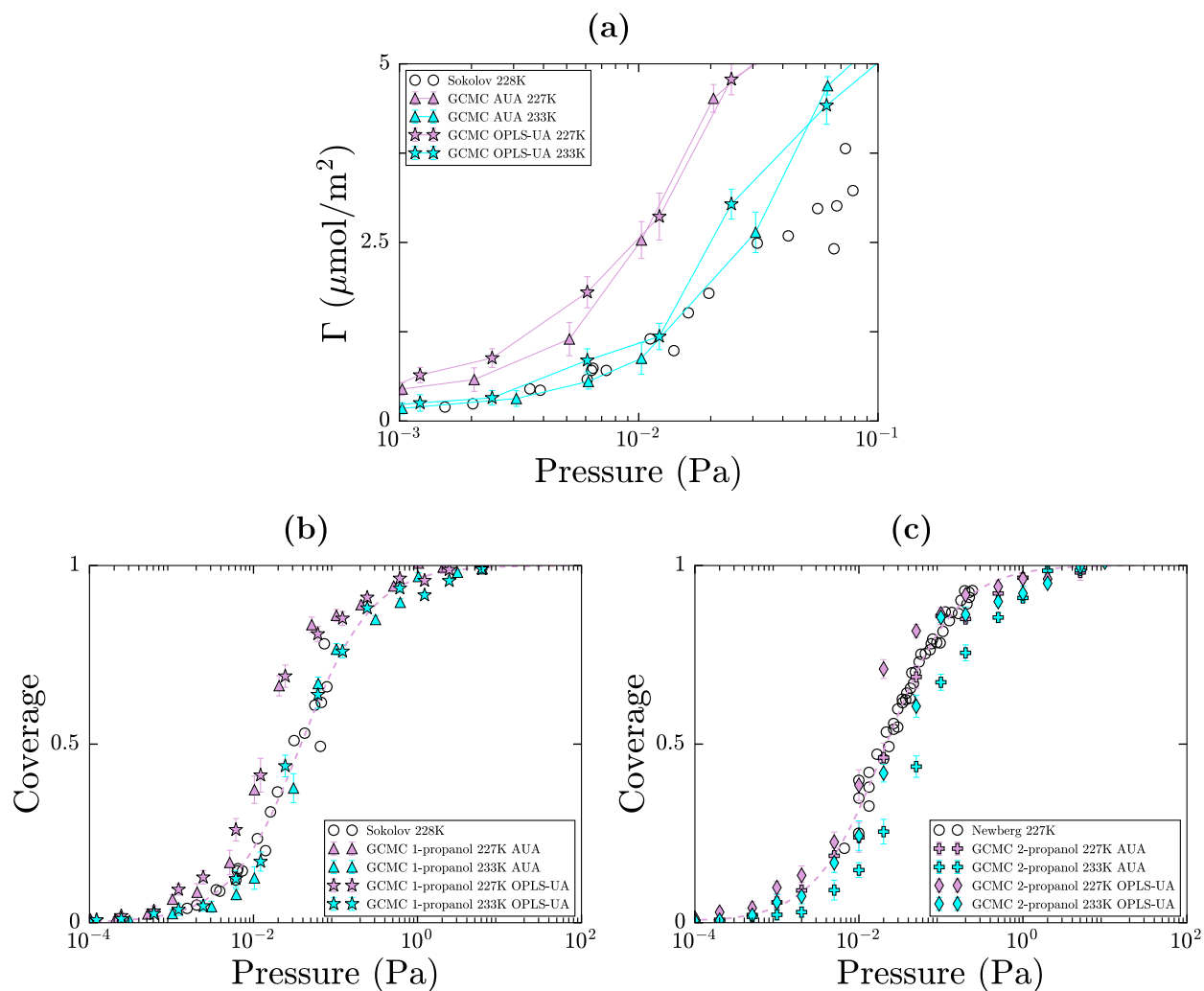


Figure 6: (a) Comparison between the experimental data (empty circles) recorded at 228 K for the 1-propanol isomer<sup>38</sup> and the adsorption isotherms simulated at 227 (pink symbols) and 233 K (blue symbols) when using the AUA (triangles) and OPLS-UA (stars) interaction potential models, in the low pressure range for which experimental data are available (lines are only guide to the eye); (b) Same as (a) on the whole pressure range investigated in the GCMC simulations; (c) Comparison between the experimental data (empty circles) recorded at 227 K for the 2-propanol isomer<sup>39</sup> and the adsorption isotherms simulated at 227 (pink symbols) and 233 K (blue symbols) when using the AUA (crosses) and OPLS-UA (diamond) interaction potential models. Note that the dotted line in (b) and (c) represents the Langmuir fit to the experimental data.

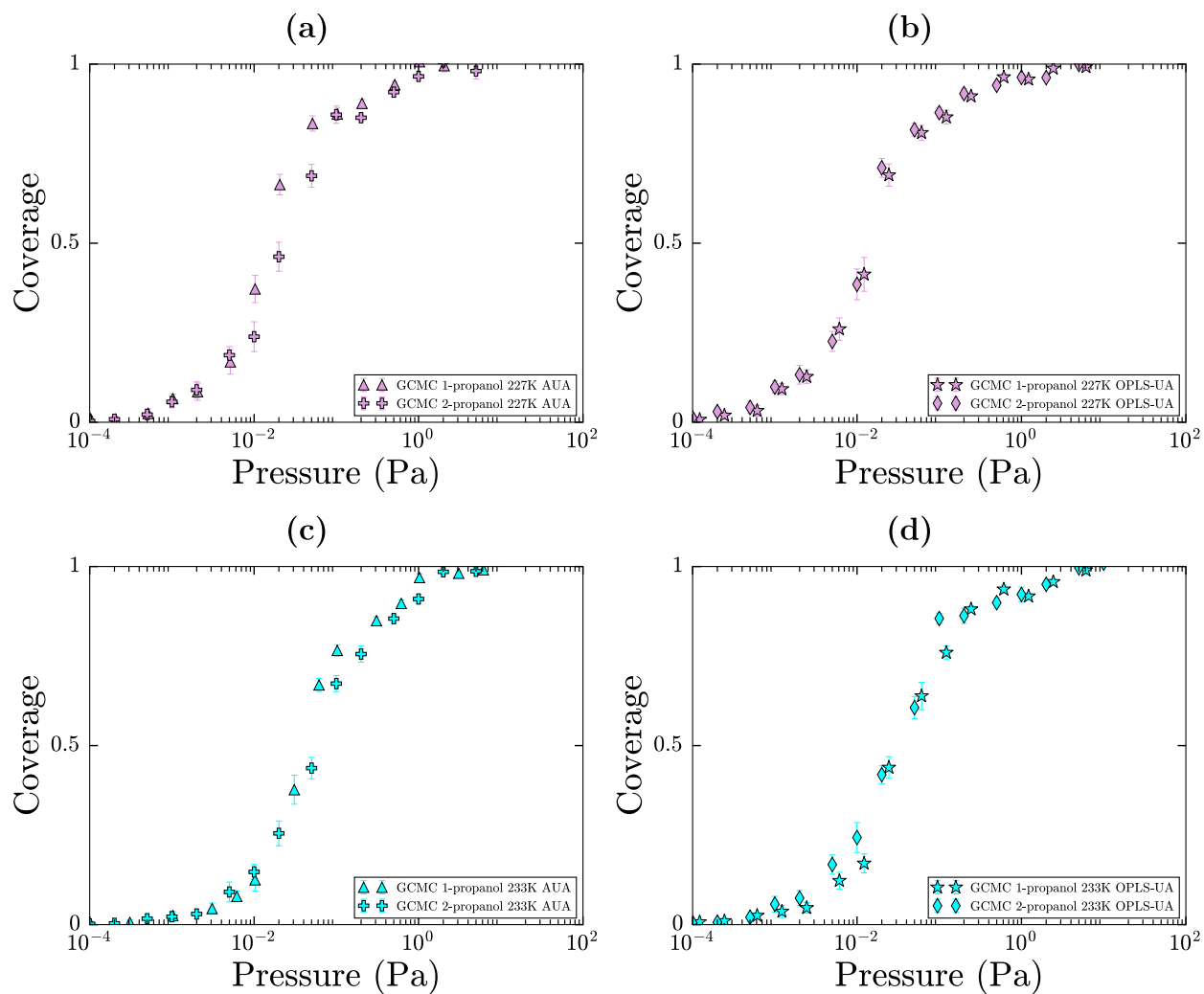


Figure 7: Comparison between the simulated isotherms for the two propanol isomers at 227 K (top row) and 233 K (bottom row), using the AUA (left) and OPLS-UA (right) interaction potential models.

# TOC Graphic

