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Reactivity of Volatile Organic Compounds at the Surface of a Water Droplet

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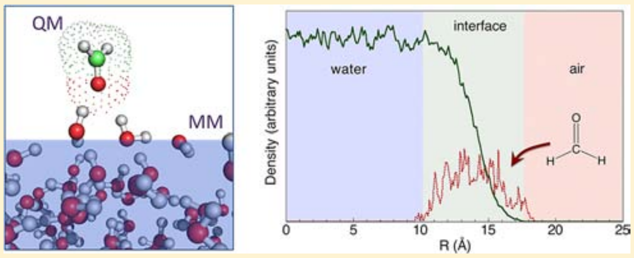
Ⓢ *Supporting Information*

ABSTRACT: Knowledge of the role of water droplets and aerosols in atmospheric chemistry is crucial to significantly improve our understanding of global warming and air quality. Chemistry at the air/water interface, in particular, is still poorly understood. There is a great need to understand how clouds and aerosols process chemistry of organics prevalent in the atmosphere. We report in this study the first computer simulation of a volatile organic compound (formaldehyde) at the air/water interface with explicit description of its ground and excited states electronic properties. We use an elaborated technique that combines molecular dynamics simulations together with a quantum/classical description of the formaldehyde—water system. We show that in spite of a large affinity for water, formaldehyde exhibits a preference for the air/water interface with respect to the bulk, roughly by 1.5 kcal/mol. Another important finding in our simulations is that frontier orbitals HOMO and LUMO undergo substantial stabilization at the interface due to surface water reorientation, which induces a local positive electrostatic potential. Such a potential is significantly larger than the one estimated in bulk water suggesting that the reactivity of formaldehyde could change with respect to both gas phase and bulk water. The conclusions presented in this work are expected to help/guide future experiments studying the chemical reactivity of volatile organic compounds at the air/water interface.



■ INTRODUCTION

A topical issue in current atmospheric chemistry is to understand heterogeneous processes and multiphase chemical reactions in aerosols and water droplets.[1−6] This is a challenging and important issue because such processes play a significant role on the overall troposphere chemical balance. The role of water clusters in atmospheric chemistry has recently been reviewed.[7] Hence, development of models accounting for such contributions are expected to provide more accurate predictions of the fate of atmospheric pollutants, in particular of volatile organic compounds (VOCs) having an impact in global warming and air quality.

Formaldehyde is one of the most abundant carbonyl-VOCs in the atmosphere[8−10] and plays a key role in the chemistry of ozone. It is a reaction intermediate in the photo-oxidation of VOCs generated by natural sources (methane, isoprene) or anthropogenic activities. Formaldehyde is also a primary pollutant produced by the incomplete combustion of many organic compounds (industry, internal combustion engines, cigarettes, etc.), or by emission from many ordinary materials (paints, adhesives, resins, particle wood, etc.). The background concentration is 0.2 ppb[11] and typical urban concentrations range between 1 and 20 ppb,[10] though greater values are observed in highly populated areas.[12]

The gas phase chemistry of formaldehyde[13] involves a fast reaction with the hydroxyl radical:

$$\mathrm{HCHO} + \cdot\mathrm{OH} \rightarrow \cdot\mathrm{CHO} + \mathrm{H_2O} \qquad (1)$$

that is followed by reaction of the ·CHO radical with O_2 to form CO and $HO_2\cdot$. In presence of nitrogen oxides, the hydroperoxyl radical oxidizes NO to NO_2 and photochemical decomposition of the latter (to NO and $O(^3P)$) followed by reaction of atomic oxygen with O_2 leads to formation of ozone. The global process can be written as follows:

$$\mathrm{HCHO} + 2\mathrm{O_2} + \mathrm{M} \rightarrow \mathrm{CO} + \mathrm{H_2O} + \mathrm{O_3} + \mathrm{M} \qquad (2)$$

The reaction with the hydroperoxyl radical $HO_2\cdot$ is potentially important too.[10] The reaction mechanism (see below) seems to involve an exothermic addition process to the carbonyl bond according to:[10,14]

$$\mathrm{HCHO} + \mathrm{HO_2}\cdot \rightarrow \mathrm{CH_2(OO)OH} \qquad (3)$$

The reaction of formaldehyde with ozone itself does not seem to play an important role, while that with the nitrate radical might be relevant in night-time processes:

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$$HCHO + NO_3 \rightarrow \cdot CHO + HNO_3 \quad (4)$$

However, the dominant reaction of formaldehyde in gas phase is thought to be the photochemical decomposition in the 250−330 nm domain according to:

$$HCHO + h\nu \rightarrow \cdot H + \cdot CHO \quad (5)$$

$$HCHO + h\nu \rightarrow H_2 + CO \quad (6)$$

Formaldehyde, on the other hand, is highly soluble in water and it is now widely accepted that it can be efficiently scavenged from the gas phase by rain and fog. The accommodation coefficient reported by Jayne et al.[15,16] is rather large, which is favored by the fact that formaldehyde is rapidly hydrated in aqueous solution to form methanediol $CH_2(OH)_2$. The gas/aqueous phase distribution estimated by the effective Henry's law constant, $H = 5020 \pm 1170$ M atm^{-1} (293 K, pure water),[17] confirms the marked affinity of formaldehyde for water. In principle, the chemistry in aqueous media can be more complex than that in the gas phase since reactions with ionic species are feasible too. In the case of hydrated formaldehyde, one generally assumes oxidation into formic acid to be the main process, and possible mechanisms are

$$CH_2(OH)_2 + \cdot OH + O_2 \rightarrow HCOOH + HO_2\cdot + H_2O \quad (7)$$

$$CH_2(OH)_2 + SO_4^{-} + O_2 \rightarrow HCOOH + SO_4^{2-}\cdot + HO_2\cdot + H^+ \quad (8)$$

The contribution of water droplets and aerosols to the whole atmospheric chemistry of VOCs is further complicated by the possible heterogeneous reactions occurring at the air/water interface.[2,6,12,18−38] The kinetics and thermodynamics of such reactions can deviate from bulk water or gas phase, as illustrated for instance by oxidation processes of trace gases by ozone and singlet oxygen in water film surfaces.[37] However, experimental studies in this field are still scarce and it is not clear, for example, whether reactions of formaldehyde at the air/water interface are related to gas phase chemistry and photochemistry (reactions 1−6) or to water chemistry with initial formation of methanediol (followed by reactions 7 and 8 and related processes). Previous computer simulations of species at the air/water interface have focused, on the other hand, on the thermodynamics aspects of the adsorption and accommodation processes, but applications to describing reaction mechanisms and molecular interactions at the interface are lacking. Adsorption at the air/water interface has also been estimated with the aid of several parametric models.[39] In summary, a full understanding of the influence of the air/water interface on atmospherically relevant chemical reactions still deserves further experimental and theoretical investigation.

Recently, we have reported a theoretical analysis[40] on the electronic properties of two important radicals, $HO_2\cdot$ and $\cdot O_2^-$, at the air/water interface. We have shown that acidity, HOMO−LUMO gap or redox potentials, for instance, are significantly different from those in gas phase or bulk. This implies that the reaction of such radicals with trace VOCs at the interface could differ from their reactivity in gas phase or aqueous solution. How this actually takes place depends on how the VOC reactivity from ground and excited electronic states is affected by adsorption at the air/water interface, and investigating this topic has major atmospheric relevance. The present study aims to shed some light on these fundamental questions providing new theoretical results that might help/guide the design of future experiments.

■ METHODS

Computer simulations on a simple but highly representative VOC, formaldehyde, have been carried out using Molecular Dynamics (MD) simulations and combined QM/MM calculations (QM/MM stands for Quantum Mechanics/Molecular Mechanics). In the simulations, formaldehyde is described quantum mechanically while a slab of water molecules is described using a molecular mechanics force-field. We allow for electrostatic embedding, which means that the Hamiltonian of the solute includes the electrostatic interaction with the solvent. In this way, polarization effects on the electronic properties of formaldehyde at the air/water interface and in bulk water can be compared. We assumed the NVT ensemble (T = 298 K) using a box containing the solute (HCHO) and 499 water molecules (TIP3P model[41]). Periodic boundary conditions are used along the X and Y directions. The solute is described at the B3LYP/6-311+G(d) (in the MD simulations) or B3LYP/aug-cc-pVTZ levels[42] (for electronic properties calculations on selected snapshots). The potential of mean force is computed using the umbrella sampling[43] and WHAM[44,45] methods. Other computational details are provided as Supporting Information.

■ RESULTS AND DISCUSSION

An important result of our MD simulations is that, in spite of its high water solubility, formaldehyde exhibits a preference for the air/water interface. This is illustrated in Figure 1 that displays molecular density and free energy profiles. The free energy difference between the bulk and the interface is estimated to be roughly 1.5 kcal mol^{-1}. The larger stability of polar molecules at the air/water interface is not unusual and has been demonstrated experimentally for different types of compounds (see for instance, refs 46−48).

As shown by the molecular density curve in Figure 1, formaldehyde moves around the interface within a layer of approximately 1 nm large. For such a layer width, specific solvation effects on solute electronic properties characterizing the interface can be anticipated.[49] Typical snapshots for different values of the interface distance are shown in Figure 2 that illustrate two important findings: (a) the formation of hydrogen bonds with water molecules at the interface, and (b) a preferential orientation of formaldehyde, the C═O group pointing toward the water surface. The analysis of average properties confirms these two findings that we discuss now in some detail.

The radial distributions functions $g(r)$ for the $O^{formaldehyde}\cdots H^{water}$ hydrogen bonds are plotted in Figure 3. In comparison with bulk water, the first peak is less intense at the interface. Indeed, the integration of the $g(r)*r^2$ function up to R = 2.5 Å (first minimum) provides an estimation of N, the number of water molecules in the first solvation shell. The calculations show a significant decrease between the bulk (N = 2.1) and the interface (N = 1.6) suggesting that the excess stability of formaldehyde at the interface is not due to higher solute−solvent interactions but probably to the modification of solvent−solvent terms (loss of solvent−solvent hydrogen bonds, solvent entropy).

Let us now look at the orientation of formaldehyde with respect to the surface. We define the Z-axis as the axis perpendicular to the water surface and θ as the angle formed between the Z-axis and the C═O bond. The calculated angular probability distribution from the simulation is shown in Figure

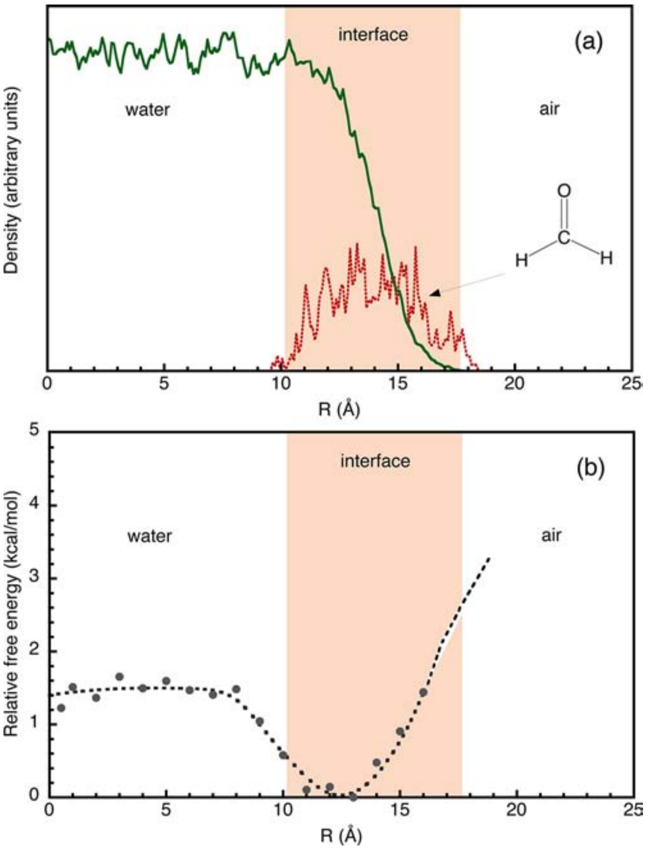


Figure 1. Preference of the HCHO molecule for the air/water interface: (a) molecular densities of water (green line) and formaldehyde (red line) from a simulation with formaldehyde freely moving at the interface, (b) bulk/interface free energy profile calculated with the umbrella sampling method. $R = 0$ corresponds to the center of the simulation box.

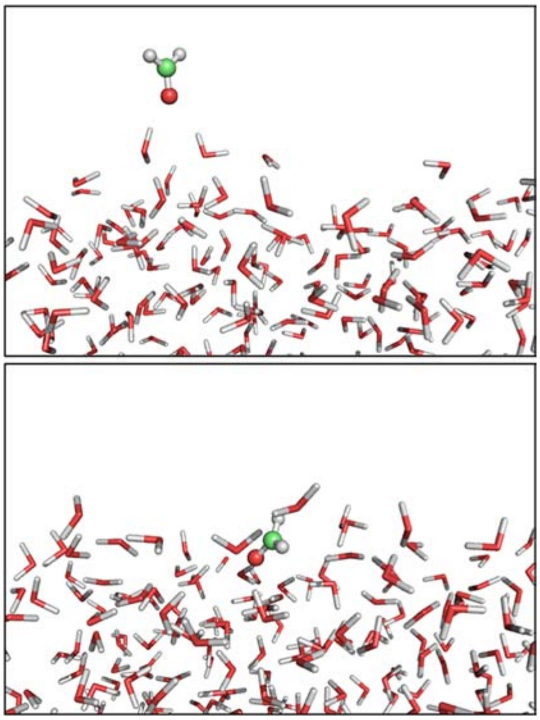


Figure 2. Typical snapshots with different values of the formaldehyde-interface distance in MD QM/MM simulations, $R = 16.55$ Å (top) and $R = 11.72$ Å (bottom). $R = 0$ corresponds to the center of the simulation box (see Figure 1).

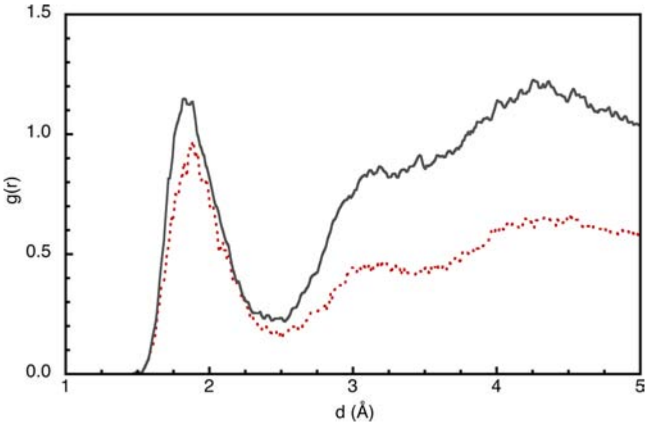


Figure 3. Radial distribution function for the $O^{\text{formaldehyde}} \cdots H^{\text{water}}$ hydrogen bond at the air/water interface (dotted red line) and in bulk water (plain black line) from MD QM/MM simulations.

4. The Figure also contains: (1) the curve associated to a regular angular distribution, simply described by the normalized $^1/_2 \sin(\theta)$ function, and (2) a typical angular distribution for a point dipole interacting with a dielectric surface. Note that in the latter case, the energy of the system depends on $\cos^2(\theta)$ according to the equation:[50]

$$W = -\frac{1}{2}\frac{\mu^2}{(2d)^3}\frac{\varepsilon - 1}{\varepsilon + 1}(1 + \cos^2(\theta)) \tag{9}$$

where d is the distance of the point dipole to the surface and ε is the relative dielectric constant.

When the solute is in bulk solvent, there is no orientational preference and the obtained θ probability corresponds, as expected, to that of a regular distribution. When the solute is at the interface, in contrast, the angular distribution clearly reveals the preference for C═O bond oriented toward the water slab (with oxygen being closer to the surface), that is, for θ values in the 0°−90° range. This distribution is clearly different from the regular one (as expected) but also different from the distribution of a point dipole interaction with a dielectric surface, which would lead to equal probabilities for values of θ and $180° - \theta$ and a local minimum at 90°. It is interesting to note that the orientation of the vector perpendicular to the HCHO plane and the Z-axis (γ angle in Figure 4) presents similar shapes at the interface and in the bulk, and in both cases, the distribution is not far from a regular one (see Supporting Information).

Solvation effects are likely to influence the electronic properties of formaldehyde at the interface and hence its reactivity. Some properties are summarized in Table 1. The average dipole moment increases from gas phase to the air/water interface by about 0.8 D. This induced dipole moment is only slightly smaller than the induced dipole moment in bulk water, which is about 1 D (a similar induced dipole moment is predicted for the water molecule in liquid water[51]).

Table 1 also contains the average energies for the frontier orbitals HOMO (n orbital) and LUMO (π^* orbital) in gas phase, at the interface and in bulk water. The HOMO−LUMO gap, which is directly connected to the nπ^* electronic transition

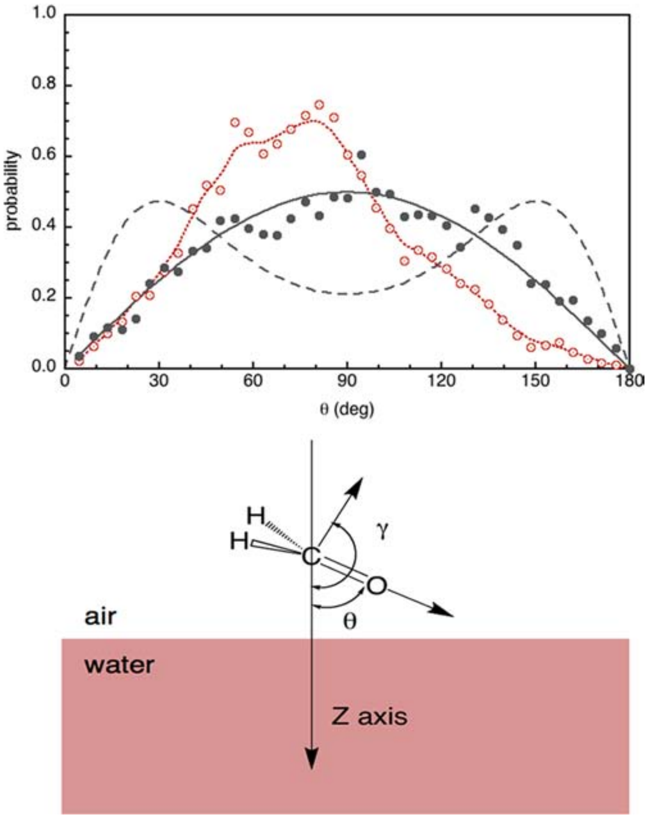


Figure 4. Angular distributions for formaldehyde in bulk solution (full circles) and at the air/water interface (empty circles). The plain line represents the regular (normalized) distribution $^1/_2 \sin(\theta)$. The dashed line represents a typical distribution for a point dipole interacting with a dielectric surface.

Table 1. Average Electronic Properties of Formaldehyde from the MD QM/MM Simulations[a]

	gas	air/water interface	bulk
μ	2.390	3.170	3.406
$\varepsilon_{\mathrm{HOMO}}$	−0.2816	−0.2934	−0.2877
$\varepsilon_{\mathrm{LUMO}}$	−0.0642	−0.0699	−0.0626
$\Delta\varepsilon_{\mathrm{LUMO-HOMO}}$	0.217	0.223	0.225
λ_1	312.9	300.8	297.7
$f_1\ 10^3$	0.0	0.0	0.0
λ_2	191.7	175.0	171.1
$f_2\ 10^3$	27.8	13.4	6.8
λ_3	170.0	157.9	154.7
$f_3\ 10^3$	38.7	51.0	60.6

[a] Dipole moment in Debyes, orbital energies in au, electronic transition wavelengths in nm, oscillator strengths in au.

energy (see analysis below), increases by 0.006 au (0.16 eV) from gas phase to the air/water interface and by 0.002 au (0.05 eV) from the interface to the bulk.

However, a fundamental difference between the interface and the bulk appears if one looks at the absolute energy of these two molecular orbitals: at the interface, the values are not intermediate between the gas and bulk but reach a minimum. Analyzing the origin of this interface effect is important because of the close relationship existing between HOMO and LUMO energies and chemical reactivity. Orbital energies in a solvated system are influenced by the electrostatic interactions with the solvent and by the solute−solvent charge transfer. The latter is not accounted for in the QM/MM model but it generally represents a small energy contribution and will be neglected in the qualitative analysis made here. The electrostatic interactions can conveniently be analyzed by making an expansion of the inhomogeneous electrostatic potential created by the solvent $V(\mathbf{r})$ around a point $\mathbf{r}_o$, taken here as the formaldehyde center of mass. At first order one gets:

$$V(\mathbf{r}) \approx V(\mathbf{r}_o) + \mathbf{E}(\mathbf{r}_o)\cdot(\mathbf{r} - \mathbf{r}_o) \tag{10}$$

The potential $V(\mathbf{r}_o)$ produces a constant energy shift of all the molecular orbitals but it does not modify the electronic distribution or the total energy of the system if the latter does not bear a net charge. The electric field $\mathbf{E}(\mathbf{r}_o)$, in contrast, produces an energy shift that depends on orbital electron densities. It polarizes the wave function stabilizing those molecular orbitals that contribute to the dipole moment of the molecule and destabilizes the corresponding antibonding orbitals. The average values of the potential and electric field at the center of mass of formaldehyde obtained in the simulations at the air/water interface and in bulk water are compared in Table 2.

Table 2. Average Values of the Solvent Potential $V(\mathbf{r}_o)$ and the Electric Field $\mathbf{E}(\mathbf{r}_o)$ at the Formaldehyde Center of Mass[a]

	$\langle V(\mathbf{r}_o)\rangle$	$\langle\lvert\mathbf{E}(\mathbf{r}_o)\rvert\rangle$	$\langle E_{\mathrm{CO}}(\mathbf{r}_o)\rangle$
Air/water interface	12.73	20.78	16.80
Bulk	8.27	24.80	18.51

[a] E_{CO} represents the electric field component along the carbonyl bond axis (10^3 au).

The average potential (zero order term) is positive in both cases, which is not surprising for a hydrogen-bond accepting system.[52] Remarkably, however, the potential at the interface is 50% larger than the potential in bulk solution and this result explains the stabilization of the HOMO and LUMO at the interface with respect to the same orbitals in bulk solution, as shown in Table 1. The electric field (first order term) is larger in bulk solution, although the relative differences are smaller (10% for the Z-component). The overall HOMO and LUMO energy shifts are a combination of both contributing terms, but clearly, the effect due to the potential predominates at the air/water interface.

Interestingly, the calculated values in Table 2 could not be deduced using a simple dielectric model; in fact, explicit consideration of specific interactions (i.e., hydrogen bonds with water) is critical. For example, in the case of an ideal point dipole interacting with a dielectric medium, the potential would be zero in bulk solution, for symmetry reasons (and according to Onsager's theory[53]), but also at the dielectric interface. In this case, the parallel and antiparallel orientations of the dipole with respect to the Z-axis (perpendicular to the surface) are energetically equivalent, as commented above, but the associated potentials have opposite signs and therefore cancel each other.

The stabilization of the HCHO frontier orbitals at the interface may have significant implications in terms of chemical reactivity. For instance, the reaction with water to form methanediol or the redox process with HO· or HO_2· (reaction 3), which also exhibit affinity for the air/water interface,[40,54,55] could undergo major modifications. These reactions have been investigated in gas phase or bulk solution using several

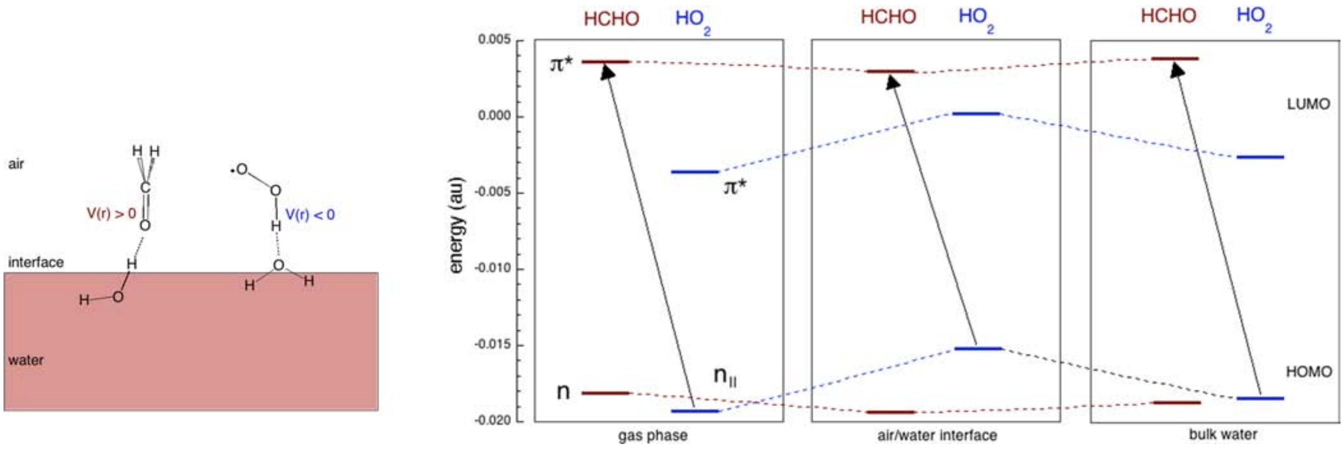
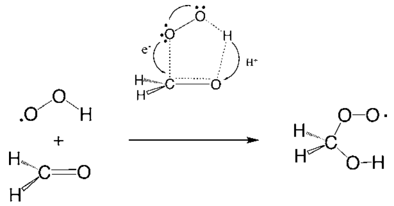


Figure 5. Schematic representation of the average HOMO and LUMO orbital energies obtained in the simulations.

theoretical approaches.[14,56−62] Though a detailed study of the possible reaction mechanisms at the air/water interface is beyond the aim of this work, it is instructive to draw a qualitative picture using simple molecular orbitals diagrams. Figure 5 displays a comparison of HOMO and LUMO energies for formaldehyde and $HO_2·$ as a function of the molecular environment. Results for the $HO_2·$ radical have been reported elsewhere[40,54,55] showing HOMO and LUMO destabilization at the interface. The reason is that the main interaction with the surface involves in that case a hydrogen bond in which the radical acts as an H-donor. This interaction induces a polarization of the surface and the creation of a negative electrostatic potential in the region of the adsorbed molecule, as schematically illustrated in Figure 5. The negative potential in turn destabilizes the molecular orbitals.

In gas phase, reaction 3 has been shown to correspond to a proton coupled electron transfer leading to formation of the $CH_2(OO)OH$ radical,[14,59] as summarized in Scheme 1. The electron transfer occurs from the doubly occupied nonbonding orbital of the radical (the in-plane $n_{||}$ orbital) to the π^* of the carbonyl group. The diagrams in Figure 5 can be used to predict qualitatively the solvation effects on this mechanism. An arrow in the diagrams indicates the orbitals involved in the electron transfer process. As clearly seen, the associated energy difference decreases in the case of the reactants solvated at the interface, as compared to gas phase or bulk water. The two latter media exhibit, in fact, quite similar diagrams. Thus, one can expect large interfacial effects on the addition reaction 3. Specifically, rate acceleration is plausible since the electron transfer process represents a major aspect of the activation process.[14,59] Obviously, other orbital−orbital interactions may come into play that should also be strongly influenced by the opposite energy shift of the formaldehyde and $HO_2·$ orbitals at the interface. Note, for instance, that the HOMO (HCHO)−LUMO ($HO_2·$) energy difference is much smaller in gas phase or bulk solution compared to the air/water interface.

Scheme 1. Schematic Representation of Reaction 3 Mechanism in Gas Phase



Solvation effects on the molecular orbitals might also imply a modification of the UV−V absorption spectrum of formaldehyde and therefore a new photochemistry at the interface (processes 5−6). It is well-known that the first excitation of formaldehyde ($n\pi^*$) is blue-shifted in bulk water, and experimentally, the shift has been estimated to be 23 nm[63] (although this value is not conclusive because of the marked trend of formaldehyde to aggregate). Solvent effects on this electronic transition have also been discussed with various theoretical approaches.[64−70] In this work, we have calculated the statistical averages of the absorption wavelengths λ and oscillator strengths f for the first three excited states. As shown in Table 1, the excitations at the air/water interface display substantial differences with respect to gas phase. In particular, they are all blue-shifted, and shifts are only slightly smaller than those found in bulk water. Note that at the interface and in bulk solution, λ_1 is not far from the tropospheric UV cutoff (∼290 nm). Oscillator strengths (for the allowed transitions) change also significantly. All these data suggest that the gas phase photochemical properties of formaldehyde should change on approaching the surface of water droplets or aerosols. In such an environment, photochemical and thermal processes can both occur although evaluation of their relative importance is not straightforward and will require further investigation. The role of roaming reactions, for which formaldehyde has been considered to be a prototypical example,[71−73] also deserves interesting studies.

■ CONCLUSIONS

The investigation has focused on formaldehyde, which is one of the most abundant carbonyl VOCs in the troposphere.

Formaldehyde, in spite of a large affinity for water, exhibits a preference for the air/water interface with respect to the bulk by roughly 1.5 kcal/mol. The calculations suggest that this free energy minimum is not due to enhanced solute−solvent interactions (the average number of hydrogen bonds is smaller at the interface with respect to the bulk). Rather, it should be connected to the decrease of favorable solvent−solvent interactions and of solvent entropy accompanying the bulk solvation process.

Solvation effects on electronic properties at the interface are noteworthy. In general, the predicted quantities are close to those calculated in bulk solution though the solvation effect at the interface is slightly smaller. For instance, the induced dipole moment is predicted to be 0.2 D smaller at the interface than in bulk water. Effects on electronic properties are associated to the value of the electric field created by the polarized solvent, which according to our simulations is smaller at the air/water interface compared to the bulk.

The most striking result in our work, however, is the fact that electrostatic interactions at the water surface can influence the chemical reactivity to a larger extent than bulk solvation. The capacity to form hydrogen-bonds with water molecules implies a preferential adsorption direction that, on average, leads to the creation of a local electrostatic potential that is larger than the potential calculated in bulk solution. This potential shifts the molecular orbital energies of the solute and therefore changes its capacity to accept or donate electrons. We have illustrated this point by looking at the frontier orbitals HOMO and LUMO of formaldehyde and those of a greatly important oxidizing species in the atmosphere, the radical $HO_2\cdot$. Another interesting finding is that the UV−V spectrum of formaldehyde at the air/water interface is quite different from gas phase, and the predicted blue shifts are comparable to those found in bulk water.

All these results put together indicate that the surface of water droplets may play a significant role on the chemistry of formaldehyde in the troposphere, influencing both photochemical and thermal reactions. Thus, one suggestion resulting from this work is that the hydration of oriented formaldehyde at the interface to form methane diol might be different from the reaction in bulk. Future simulations will address identifying the associated reaction mechanisms and dynamics. However, clarifying the role of chemistry at the air/water interface will also need advances in experimental methods to allow direct experimental measurements of the reaction kinetics.[25,36,74,75]

■ ASSOCIATED CONTENT

Supporting Information

Details on methods and the distribution of γ angle for formaldehyde in bulk solution and at the air/water interface. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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