

# Interfaces Select Specific Stereochemical Conformations: The Isomerization of Glyoxal at the Liquid Water Interface

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## Supporting Information

**ABSTRACT:** Interfacial chemistry involving glyoxal at aerosol surfaces is postulated to catalyze aerosol growth. This chemistry remains speculative due to a lack of detailed information concerning the physicochemical behavior of glyoxal at the interface of atmospheric aerosols. Here, we report results from high-level electronic structure calculations as well as both classical and Born–Oppenheimer ab initio molecular dynamics simulations of glyoxal solvation at the air/liquid water interface. When compared to the gas phase, the trans to cis isomerization of glyoxal at the liquid water interface is found to be catalyzed; additionally, the trans conformation is selectively solvated within the bulk to a greater degree than is the cis conformation. These two processes, i.e., the catalytic effect at the water interface and the differentially selective solvation, act to enhance the concentration of the cis isomer of glyoxal at the water interface. This has important consequences for the interpretation of experiments and for the modeling of glyoxal chemistry both at the interface of water clouds and at aerosols. Broader implications of this work relate to describing the role of interfaces in selecting specific stereo molecular structures at interfacial environments.

Glyoxal has recently been suggested as a possible catalyst for aerosols growth in the atmosphere.<sup>1</sup> At present, the understanding of aerosol chemistry remains poor; this lack of understanding results in the fact that atmospheric aerosol nucleation and growth are a large source of uncertainty in weather and climate predictions.<sup>2</sup> Anthropogenic sulfur-based compounds have been indicted as a major ingredient for the nucleation of new aerosols.<sup>3</sup> However, new reports<sup>4,5</sup> have shown aerosol nucleation and growth in unpolluted areas with high concentration of oxygenated organic molecules, further stating our poor knowledge of the molecular level processes underlying the interaction between aerosols and atmospheric trace gases. Glyoxal is an oxygenated organic compound present as a result of anthropogenic and biogenic emissions<sup>6</sup> and, once hydrated, can strongly bind sulfates.<sup>7</sup> Moreover, preliminary evidence shows that glyoxal can even be hydrolyzed in the presence of a small number of water molecules, suggesting that it can enhance both the water uptake on inorganic aerosols and the growth of the aerosol.<sup>8</sup> However, all

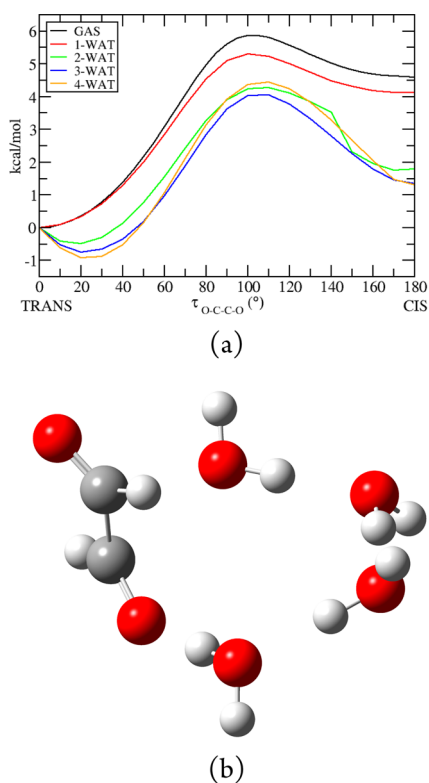
these processes are speculative due to a lack of detail information about the physicochemical behavior of glyoxal at the interface of atmospheric aerosols.

In this study, we have investigated the interaction of glyoxal at the air/liquid water interface by employing both a set of high-level electronic structure calculations as well as classical and Born–Oppenheimer ab initio molecular dynamics (AIMD) simulations. Our results show that when glyoxal is adsorbed at the liquid water interface, the trans to cis isomerization is catalyzed by the interface with references to the gas phase or in small water clusters. Moreover, molecular dynamics results show that the trans isomer can be absorbed more easily into the bulk than is the cis; the cis isomer prefers to reside at the interface. The catalytic effect of the interfacial water environment on glyoxal isomerization and the different surface propensity of the two isomers can, therefore, lead to an enhancement of glyoxal in its cis form at the water interface. Because glyoxal is generally assumed to be in its trans form in the gas phase and at interfacial environments,<sup>7–13</sup> the results of this work has important implications in the experimental interpretation and modeling of glyoxal chemistry at the interface of water aerosols in the atmosphere. Moreover these findings suggest that water interfacial environments display the property of specifically selecting for individual stereo forms at the interface/bulk.

As a preliminary step, we investigated the interaction of glyoxal with water. We observe the isomerization profile in both the gas phase and in small water clusters. Figure 1a reveals the results of a full optimization at B3LYP/6-311++g(3df,3pd) level,<sup>14,15</sup> scanning different values of the glyoxal torsion O–C–C–O angle,  $\tau$ . This level of theory has been already successfully employed in the study of the interaction between glyoxal and single water molecules;<sup>8</sup> this method was validated herein by comparing the isomerization profiles in the gas phase among several higher order theories (Figure 1S in the Supporting Information). As illustrated in Figure 1, in the gas phase the trans isomer ( $\tau = 0^\circ$ ) corresponds to the minimum of the energy profile along the  $\tau$  coordinate and there is a rotation barrier located at  $100^\circ$  on the order of 6 kcal/mol. The location and height of this barrier agrees with previous computational and experimental values for the isomerization of glyoxal within

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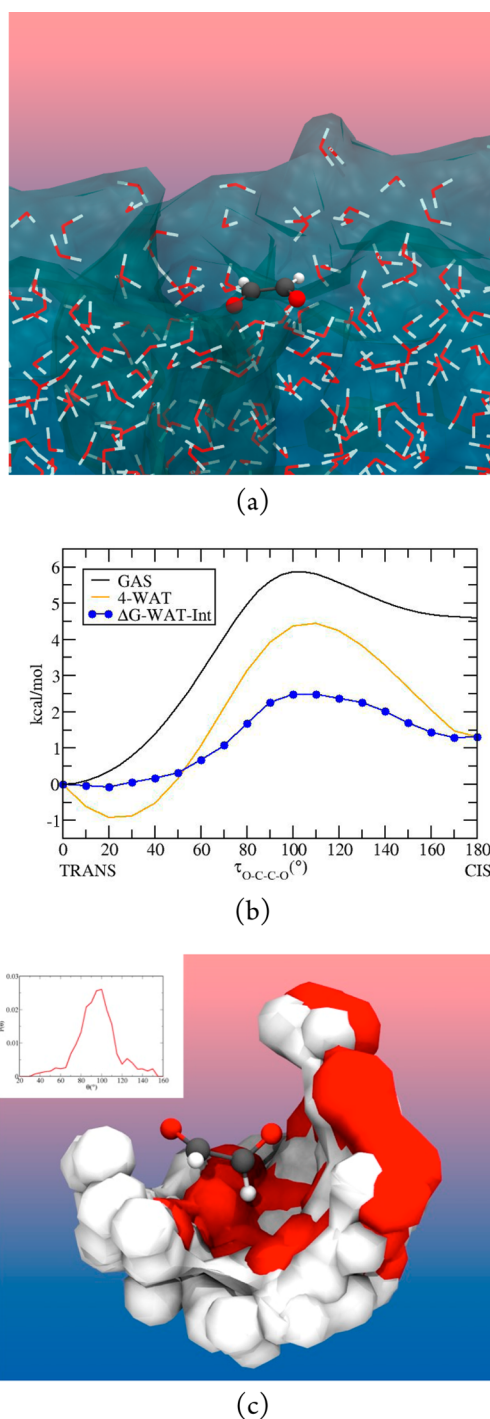


**Figure 1.** Panel a: relative energies at different torsion angle,  $\tau$ , obtained from electronic structure calculations in vacuum. Panel b: snapshot of glyoxal in 4 water cluster at the energy minimum, i.e.,  $\tau = 20^\circ$ .

the gas phase.<sup>10–12,16</sup> Shifting from the gas phase by the addition of two water molecules is sufficient to lower the transition barrier to 4.5 kcal/mol; further increasing this to 3 and 4 water molecules, the energy minimum shifts to  $\tau = 20^\circ$ . Figure 1b shows the corresponding structure in this minimum at  $\tau = 20^\circ$  for the case of the 4-water cluster. In clusters composed of 3 and 4 waters, the minimum structure is a slightly tilted trans isomer with the formation a hydrogen-bound water ring attached to one glyoxal oxygen while the other oxygen is pushed backward, breaking the O–C–C–O  $sp^2$  torsional plane.

Figure 1a suggests that the presence of small clusters of water and, by extrapolation, water aerosols and droplets, have a catalytic effect on glyoxal isomerization. We employed a series of AIMD simulations<sup>17</sup> to explore further this effect on the surface of liquid water. By initially placing a glyoxal molecule on the top of a water slab composed of 216 water molecules (Figure 2a), we calculated on-the-fly the forces driving the dynamics using density functional theory. AIMDs based on density functional theory are capable of accurately describing the interactions between solute and solvent molecules, while additionally permitting a change of the torsion angle during these dynamics.<sup>17</sup> In this work, the BLYP<sup>14,18</sup> functional with Grimme correction<sup>19</sup> was used. This AIMD setup was already successfully employed in the modeling of liquid water interfacial environments.<sup>20,21</sup> Additionally, our AIMD setup was benchmarked using the isomerization profile of glyoxal in the gas phase as a reference (Figure S1 and AIMD setup details in the Supporting Information).

In preliminary AIMD runs lasting 28 ps at 300 K, no isomerization events were observed; this observation remained



**Figure 2.** Panel a: snapshot from the AIMD trajectory. Water surface is showed for clarity by triangulating on the water coordinates. Panel b: Free energy profile (blue curve) for the trans to cis isomerization at the liquid water interface obtained by AIMD/TI. The black and yellow curves are the relative energies for isomerization in the gas and 4-water cluster, respectively. Panel c: Position of the water oxygen (red) and hydrogen (white) every 10 steps of the 5 ps trajectory constraining  $\tau = 100^\circ$  after referring the trajectory on glyoxal frame of reference. In the inset, the angular distribution between the interfacial normal and glyoxal C–C vector for the same trajectory.

true independent of initial conformation (see Figure S2 and the two trajectory movies contained within the Supporting Information). This supports the fact that the cis and trans configurations are local minimum of the free energy and that a

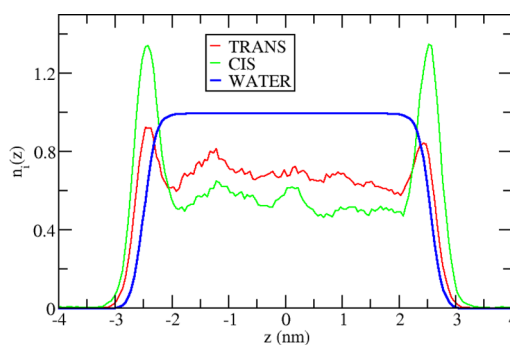
trans-to-cis transition (or vice versa) is likely to not be observed within the few ps time-scale of an expensive AIMD run. For this reason, we employed thermodynamics integration<sup>22</sup> (TI) methods to study the free energy cost required to transit the rotational barrier, reconstructing the free energy profile along the reactive coordinate defined by the torsion angle  $\tau$ . We performed 19 AIMD runs of 5 ps while parametrizing the torsional angle, i.e., constraining the torsion angle to different values. The free energy profile was constructed by considering the applied bias potential and removing the first 1.5 ps of equilibration time from each run.

Figure 2b shows (in blue) the free energy profile for glyoxal isomerization at the liquid water–air interface at 300 K obtained by AIMD and TI. Within Figure 2b, the black (yellow) curve represents the gas phase (4-water cluster) potential energy surface for glyoxal along the  $\tau$ -coordinate: the rotational barrier for water cluster and at the liquid water interface are  $\sim 4.5$  and  $\sim 2$  kcal/mol, respectively; each value lower than that experienced in the gas phase. Upon closer inspection, Figure 2b suggests a much higher cis/trans relative concentration at the interface compared to the gas phase due to the  $\sim 3$  kcal/mol lowered free-energy well for the cis isomer. Interestingly, one of our AIMD simulations of glyoxal in a vacuum shows an isomerization event occurring at 4.5 ps (Figure S3), supporting the idea that the cis conformation could be more stable at the liquid water–air interface. This observed event and the small energy difference for the cis-to-trans barrier calls for some caution concerning possible stabilization effects of the cis isomer at the liquid interface compared to the gas phase.

Figure 2c shows the location of the water oxygen (red) and hydrogen (white) every 10 steps along the 5 ps trajectory after referring the coordinates of the trajectory constrained at  $\tau = 100^\circ$  on the glyoxal frame of reference. Comparing this figure, that of the 4-water cluster (Figure 1b) water not only constrain one aldehyde group but simultaneously favor the rotation of the other group; this is suggestive of a possible explanation for the observed catalytic effect at the interface. Indeed, the hydrogen bond network between glyoxal and water could favor the breaking of the strong intramolecular O–H interaction while stretching the oxygen lone pair, lowering the transition barrier. This description is also supported by Figure 2a, showing both aldehyde groups embedded and hydrogen bonded by interfacial waters. Moreover, the probability distribution of the angle between the interface and the glyoxal C–C vector shows a peak at about  $90\text{--}100^\circ$  (see inlay of Figure 2c). This implies that glyoxal is, indeed, lying down on the interface with both aldehyde groups interacting with water.

Additionally, it is also interesting to note from Figure 2b that in the gas phase there is a clear global minimum at  $\tau = 0^\circ$ ; however, in the interface case, this once distinct minimum becomes shallow and is shifted to  $\tau = 20^\circ$ . In the 4-water cluster, this  $20^\circ$  minimum is more defined and correspond to the formation of an ordered water ring around the aldehyde group (Figure 1b). This structural arrangement, even if energetically convenient, could be entropically unfavorable at the liquid water interface, thereby explaining the shallow minimum. It is worthwhile to note, since thermodynamic integration is computed from MD at finite temperature, it considers this entropic contribution. In opposition, this entropic term is not accounted in the electronic structure calculation performed at 0 K.

Classical MD simulations addressed the question of differential propensity of glyoxal to exist at the surface vs the bulk of liquid water. In classical MD simulations, forces are calculated from empirical potential functions; for this reason, classical MD simulations are, in general, not capable of properly modeling the isomerization process. Moreover, classical MD simulations are computational cheaper and are, thusly, capable of longer sampling times, which are useful in the determination of interfacial propensity and preference. Two MD runs, each of 75 ns, were performed: one for the trans isomer and the other for the cis isomer. The MD setup employed here is similar to those in previous studies of surfactants on liquid water slab,<sup>23–25</sup> an explicit record of the simulation initialization is reported in the Supporting Information. Figure 3 shows the probability



**Figure 3.** Probability distribution for the center of mass position of the trans (red) and cis (green) isomer along the coordinate perpendicular to the water interface. The blue curve reports the water profile in arbitrary units.

distribution of glyoxal's center of mass position of along the coordinate perpendicular to the water surface for each the trans and the cis isomer. The blue curve indicates the liquid water profile for a slab formed by 4142 water molecules with the two vacuum–liquid water interfaces at about  $\pm 3$  nm. The probability distributions shown in Figure 3 state that the cis conformation is more preferentially located at the interface than the trans isomer whereas the trans form can be more easily solvated into the bulk. This implies that the cis/trans relative concentration can be enhanced in favor of the cis isomer at the interface, even if the trans is more energetically favorable.

The portrait for glyoxal adsorption and solvation at the liquid water interface in this work is suggestive of important implications, which can affect the interpretation of chemical mechanisms occurring on the surface of liquid droplets. Within the gas phase, the trans isomer is the most energetically favorable conformer for glyoxal. These gas phase findings are consistent with those of observations from the literature.<sup>9–12</sup> However, our new results seem to state clearly that the water interface can catalyze the trans to cis isomerization by reducing the barrier to rotation by several kcal/mol; additionally, this preferential barrier location has been found to energetically stabilize the cis isomer. Several experiments and computational studies present in the literature<sup>7–13</sup> assume that glyoxal resides mainly in its trans form in the gas phase, as well as, at interfacial environments. However, our findings suggest that both isomer forms are likely to be present at the surface of liquid droplets and aerosols. Moreover, results from our MD simulations indicate that the trans isomer is more likely solvated into the bulk than the cis isomer, suggesting an additional mechanism that can increase the relative concentration of the cis isomer at



the interface. In summary, there are two processes that act to favor the cis isomer form of glyoxal at the liquid water interface: first, the catalyzed isomerization at the interface and second, is the selective solvation in the bulk of the trans form over the cis one.

This work suggests a surprising property of interfacial environments, explicitly the selecting of specific stereo molecular structures at the interface. As we have seen in this work, the heterogeneity of the interfacial environment can (a) catalyze stereo structural changes, (b) stabilize and (c) selective solvate one structural form with respect to the other at the interface or in the bulk. Here we reported the specific case of glyoxal at the liquid water interface; however, conformational selectivity is likely to be a more general property of other interfacial environments, valid for larger classes of molecular species. Future work is planned to shed more light on this phenomenon and to also expose any connection between this phenomenon and the electrostatic surface potential at the liquid water interface.<sup>16,26,27</sup>

## ■ ASSOCIATED CONTENT

### ● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI 10.1021/jacs.6b10208

Molecular Dynamics set up and benchmark (PDF)

Trajectory movie (MPG)

Trajectory movie (MPG)

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### Notes

The authors declare no competing financial interest.

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