A Bit of Sugar on TiO_2: Quantum Chemical Insights on the Interfacial Interaction of Glycolaldehyde over Titanium Dioxide

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Abstract

Among 200 molecules discovered up to now in the interstellar and circumstellar space, glycolaldehyde (GA) represents the smallest monosaccharide detected in those places. This detection comes with important clues about the origins of life in the Universe and in a primeval Earth, as GA is one of the intermediates in the formose reaction leading to ribose. Mineral surfaces, such as TiO_2, have a primary role in processing simple molecules toward more complex prebiotic species. In the present work, the adsorption of GA over the surface of TiO_2 anatase (1 0 1) is investigated by quantum chemical simulations, being this the first step involved in the series of reactive steps mediated by the surface. Six adsorption configurations are modeled by periodic density functional theory (DFT) calculations, and for each of them structural, energetic and vibrational properties are calculated. The results of the theoretical study are supported with measurements of the GA adsorption on TiO_2 by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, in order to gain experimental evidences about their interaction. The outcomes show that the most stable adsorption configuration of GA on TiO_2 involves the anchoring through both the OH and the C=O groups, with a binding energy of about 18 kcal mol^{-1}. In addition, GA can be activated by the interaction with the surface, which may lead to the formation of reactive species that, in turn, can undergo further chemical processing.

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Introduction

Glycolaldehyde (GA) has received a good bit of attention recently mostly due to its detection in space and from the related experimental spectral characterization. Interstellar GA has been first detected by Hollis et al. toward the Galactic center source Sagittarius (Sgr) B2(N) on the basis of six millimeter-wave rotational transitions of the lowest energy conformer, albeit some of them were only partially resolved.[1] This pioneering observation has been subsequently confirmed first by Halfen et al.[2] and then by Requena-Torres and co-workers.[3] Further, by means of interferometric sensing measurements of the Sgr B2(N) region, it has been also shown that, at variance with its structural isomers methyl formate and acetic acid, GA has a large spatial scale (60").[4] Few years ago, Beltrán et al. have reported the first detection of GA toward the hot molecular core G31.41+0.31, a very massive star forming region located outside the galactic center.[5] Finally, GA has been discovered within the protostellar binary IRAS 16293-2422, a solar-type young star, by means of the ALMA (Atacama Large Millimeter Array) interferometric observatory.[6]

The importance of detecting GA in astronomical objects, and in star forming regions in particular, can be traced back to its structural chemical formula, CH_2OHCHO (see Figure 1) that makes this molecule to be considered as the smallest monosaccharide, of general composition $(CH_2O)_2$. This molecule is related to the origin of life, since it is the first intermediate in the formose reaction[7,8] that, under the conditions of the primeval Earth, leads to the catalyzed synthesis of sugars up to ribose. In this process, the parent molecule is formaldehyde (H_2CO) that produces GA through a 1 + 1 carbon addition and then successive additions of H_2CO provide a route to ribose. Hence, GA appears a key ingredient for the production of three-, four- and five-member sugars.[9] On this basis, it is clear that the astronomical detection of GA comes along with important and fascinating clues about the chemical processes that lead to the formation of biologically relevant molecules already in space and in star forming regions, this being strictly related to the exogenous hypothesis about the origins of life.[10-12] On the one hand, the relative abundance ratios of methyl formate : acetic acid : glycolaldehyde in Sgr B2(N) have been estimated to be 26 : 1 : 0.5.[4] On the other, it has been proposed that the astrochemical synthesis of GA requires the processing on the surface of dust grains, since "there exist no gas-phase chemistry models that can explain the formation of large interstellar molecules such as glycolaldehyde",[13] a statement that is supported by laboratory experiments to some extent.[14-16] In particular, Woods et al. have tested five possible astrochemical reaction mechanisms,[17] two taking place within the grain mantle, two on the grain surface and one-gas phase scenario, speculating that the last one appears unlikely. Rather, the two most effective pathways leading to GA have appeared those involving the radical reactions within the grain mantle promoted by UV radiation and the surface mediated reaction between H_3CO and HCO (actually methanol and formaldehyde derivatives), proposed by Sorrell[18] and Beltrán et al.[5] respectively. More recently, thanks to the support of quantum chemical calculations, an undiscovered grain-surface reaction mechanism has been proposed, that involves the dimerization of the formyl radical, which would be favored from both the availability of adsorbed HCO and the small activation energy barrier due to H atom tunneling.[19]

Besides its astrochemical and astrobiological relevance, GA is also of atmospheric interest, indeed, it belongs to the family of oxygenated volatile organic compounds (OVOCs) and it has been proposed to be involved in the formation of aqueous-phase secondary aerosols.[20] GA is directly produced during biomass burning[21] and it is also an intermediate in the oxidation of gas phase organic compounds.[22-28] Because of this twofold relevance, GA has been the subject of several experimental and theoretical studies. The first investigation about its rotational spectrum was carried out in the frequency region below 25 GHz.[29] In 2001 a larger number of rotational transitions through 354 GHz has been measured using two different spectrometers, one relying on Stark modulation, the second using FASSST (Fast Scan Submillimeter Spectroscopic Technique).[30] About ten years later, the laboratory spectrum of glycolaldehyde has been measured and analyzed in selected frequency ranges across the sub-millimeter range up to 1.2 THz.[31] More recently, the pure rotational spectra of glycolaldehyde isotopologues have been recorded from 6.5–20 GHz and 25–40 GHz by using two pulsed-jet chirped pulse Fourier transform microwave spectrometers.[32] Concerning the infrared (IR) region, very recently, the medium IR spectra of gas-phase GA have been investigated in detail, and the analysis has led to the band assignment and determination of absorption cross sections, which have been in turn employed to detect and quantify GA in atmospheric biomass burning emissions.[20] Further, long before, the vibrational spectra of the different conformers of GA in low temperature noble gas matrices were reported with the aim of studying IR induced and thermal conformer interconversion processes.[33] On the theoretical side, anharmonic frequencies and IR intensities in the mid-infrared region for the four conformers of glycolaldehyde were obtained from hybrid coupled cluster/density functional theory (DFT) force fields by applying a variational-perturbational scheme.[34]

Titanium dioxide (TiO_2) is one of the most versatile and widespread materials, that over the years has found a broad range of applications, from pigments, paints and cosmetics up to catalysis, energy production and water splitting.[35,36] On the environmental side, TiO_2 is employed for the production of photo-catalytic cements and self-cleaning coatings as well as bio-active panels and tiles, which are able of purifying air from atmospheric pollutants.[35,37] What is perhaps less known about titanium dioxide is that it is one of the potential cosmic dust minerals in oxygen rich dusty environments[38,39] and, based on thermodynamic considerations, it has been inferred that titanium oxide molecules can survive to the physical conditions around some stars, and then act as aggregation nuclei for other particles such as silicates and icy mantles.[40]

Surface enhanced chemistry is not only important to understand and explain the formation of complex organic molecules in space, but it appears to play a fundamental role for their assembly toward more complex biochemical building blocks.[41-43] Indeed, the activity of mineral surfaces, including TiO_2, has been demonstrated to promote the synthesis of simple biomolecules, starting from prebiotic species.[44] As for TiO_2, very recently Martra and coworkers have shown that this substrate catalytically promotes the polymerization of glycine, with oligomers containing up to sixteen units, by successive feeding with monomers from the vapor phase.[45] Further, it has also been demonstrated that anatase nanoparticles can activate carboxylate groups toward nucleophilic attack by amines to give amides,[46] and almost meanwhile, Leyton et al.[43] illustrated the role of both rutile and anatase in pushing up the thermal synthesis of the glycine-L-glutamine polymer, either with and without UV light irradiation.

In order to provide understanding on the chemistry involved in surface-enhanced processes that have potentially preceded life's origin, it appears important to explore in detail the single molecular events ruling the interaction of prebiotic molecules with different mineral surfaces. With these premises, in this work the adsorption interaction of GA on TiO_2 is investigated theoretically by means of quantum chemical calculations rooted into DFT, adopting the periodic approach and atom-centered Gaussian basis sets. Theoretical predictions are then compared with the infrared spectra of the adsorbed molecule, obtained experimentally by Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy measurements. The work is structured as follow: computational and experimental details are described in Sections 2 and 3, respectively, results are presented in Section 4 and finally conclusions are addressed in Section 5.

2. Quantum Chemical Calculations

The adsorption interaction of GA over TiO_2 was simulated by means of periodic quantum chemical calculations carried out by using the Crystal14 suite of programs.[47-49] A preliminary screening of the possible adsorption configurations of GA were carried out by using a 6-layer atomic slab cut from the anatase bulk along the (1 0 1) plane and extending in the *x*-*y* directions,[50] with the cis-cis conformer of GA (see Figure 1) being considered as it is the most stable[34] and the only one observed in the gas phase.[20] Starting from the obtained structures, calculations were refined by using a 12-layer atomic slab, with a surface area of 19.9 Å^2, cut along the same crystallographic plane. This surface was selected since it is the anatase most stable one and hence it should be the most exposed for the adsorption. In order to keep the symmetry of the simulated systems as high as possible, GA molecules were adsorbed on both the sides of the slab, and during the calculations, the Hamiltonian matrix was diagonalized at 7**k** points within the first Irreducible Brillouin Zone (IBZ) adopting the Monkhorst-Pack net sampling.[51] The level-shifting (0.7 Ha) method was employed and the Fock/KS matrix at a given iteration was mixed with 30% of the previous one.[47]

For each adsorption model simulated, geometry optimization was carried out first, and then, at the optimized structure harmonic vibrational frequencies were calculated at the Γ point of the IBZ through analytic evaluation of the Hessian matrix.[48,49] For geometry optimizations and frequency calculations, the Ti and O atoms were described by means of the 86-51G* and 8-411G contractions, respectively.[52] The pc-1 basis set[53,54] (downloaded from the EMSL basis set exchange library[55]) was employed for describing the GA molecule, as it delivers reasonably accurate results for vibrational properties, while reducing the computational cost with respect to other double-ζ basis functions.[56] Single point energy calculations were performed at the obtained equilibrium structures by adopting larger basis sets, and the resulting adsorption energies were corrected for the basis set superposition error (BSSE) that arises from the basis set incompleteness, resorting to the counterpoise procedure introduced by Boys and Bernardi.[57] Specifically, the TiO_2 surface and the GA molecule were described by the pob-TZVP[58] and cc-pVTZ[59-60] basis sets, respectively. In order to lighten the notation, from now on, only the basis set employed for the molecule will be indicated when referring to the model chemistry.

All the calculations were performed adopting the B3LYP[61,62] functional augmented by dispersion correlation effects by means of the DFT-D2 scheme, introduced by Grimme[63] and implemented within the Crystal code. During the last years it has been deeply demonstrated that DFT is unable to account for dispersion correlation effects (see e.g. Refs. 64-70 and references therein) though their inclusion is fundamental for correctly describing the energetic of molecular complexes, chemical reactions in general, and adsorption processes as well.[71-73]

In addition, for the gas-phase molecule, geometry optimizations and calculations of anharmonic frequencies and intensities were carried out at different levels of theory, specifically B3LYP and M06-2X[74] coupled to the pc-1 basis set and B2PLYP[75] in conjunction with cc-pVTZ. Vibrational properties beyond the harmonic approximation were derived in the framework of a general VPT2 engine[76] as implemented in the Gaussian 16 suite of programs.[77] In order to tackle the problem of resonances plaguing the VPT2 approach, the generalized second-order vibrational perturbation theory (GVPT2) was adopted.

3. Experimental details

DRIFT spectra of GA adsorbed on TiO_2 were recorded in the medium IR region by using a Bruker Vertex 70 FTIR spectrometer equipped with a DTGs (deuterated triglycine sulfate) detector, a globar source and a KBr beamsplitter. The Harrick Scientific Praying Mantis diffuse reflectance accessory, which was mounted inside the sample compartment of the spectrometer, was fitted with a stainless steel high temperature reaction chamber (Harrick Scientific HVC-DRP-5). The chamber is enclosed by a dome with three windows, two of which are made of KBr for letting the IR radiation to be transmitted, whereas the third one, made of quartz, can be employed to view or UV irradiating the sample. The temperature inside the reaction chamber can be set through the sample stage which is temperature controlled by a cartridge heater. Further details of the experimental apparatus can be found in previous papers.[73,78]

At room temperature and atmospheric pressure GA exists in the form of its dimer (2,5-dihydroxy-1,4-dioxane), that is a six member ring with a 1,4-dioxane structure, which can be purchased as a white crystalline powder (Sigma Aldrich), with a melting point between 80 and 90 °C depending on the stereoisomeric composition and a vapor pressure of about 4 Pa. In order to let the sample enter the environmental chamber, about 10 mg of solid compound were put in a reactor vessel and heated at the temperatures of either 85 or 95 °C and adsorption experiments were carried out at both these temperatures.

Since titanium dioxide does not transmit the IR radiation below about 1000 cm^{-1}, mainly because of the strong absorptions due to Ti—O stretching, the TiO_2 substrate (Degussa P25, 80% anatase and 20% rutile) was diluted with KBr, which represents an optically non-interfering matrix and further it minimizes the unwanted effects due to specular reflection.[79] The measurements were carried out by using different concentrations of TiO_2, ranging from 10% to 100% (w/w), albeit as expected, in the latter case the signal-to-noise ratio below 1100 cm^{-1} became too low. In order to make the experiments reproducible, and hence to expose different amounts of GA to TiO_2 surfaces with the same acid/base features and adsorption sites, the solid substrate was treated at high temperature (350 °C) under dynamic vacuum for 2 hours and then it was re-oxidized with a mixture of O_2/N_2. The treated surface was used as background for the recording of the spectrum of the adsorbed gas. In addition to the spectra of GA in the presence of TiO_2 as substrate, the spectra of free GA were recorded by using a non-adsorbing substrate composed of pure KBr, over which molecules do not adsorb. All measurements were performed at a resolution of 4 cm^{-1} with the reflectance spectra resulting from the Fourier transformation of 128 co-added interferograms.

4. Results and Discussion

The GA molecule in its most stable configuration (Figure 1) is an asymmetric rotor belonging to the C_s symmetry point group, with the symmetry plane defined by the two carbon atoms, the carbonyl oxygen and the hydroxyl group. The latter is involved in an intramolecular hydrogen bond with the carbonyl that is responsible for the largest stability of this conformer. The molecule possesses eighteen normal modes of vibration classified, in terms of symmetry species, as either A' (ν_1 - ν_{12}) or A'' (ν_{13} - ν_{18}) that give rise to hybrid *a*/*b* or *c*-type absorption bands, respectively. Experimental and theoretical transition wavenumbers are reported in Table 1.

Although out of the aim of this work, prior of describing the outcomes for adsorption simulations, it can be instructive to compare experiment and theory for the free molecule, as detailed in Table 1. Inspection of this table reveals that the M06-2X functional fails in computing the anharmonic corrections for the normal modes ν_{12}, ν_{17} and ν_{18} with meaningless values of anharmonic constants. Conversely, the B3LYP and B2PLYP functionals perform sensibly better with mean absolute deviations of 24 and 8 cm^{-1}, respectively, the maximum positive (negative) deviations being 50 (–50) cm^{-1} for the former and 28 (–18) cm^{-1} for the latter.

Exploratory simulations of the adsorption of GA on TiO_2-anatase (1 0 1) have been carried out by using a six-layer slab according to seven different adsorption configurations, namely cI – cVII. These differ for the functional groups involved in the interaction with the substrate as well as for the orientation of the GA molecule with respect to the surface (see Figure S.1 of Supplementary Material). Configurations cI to cVI have been thought as non-dissociative interactions: cI features GA pointing both the hydroxyl hydrogen and the carbonyl oxygen toward anatase with its symmetry plane perpendicular to the surface. In cII the symmetry plane is still oriented in the same way as cI, but now only C and H atoms face on the surface. In cIII and cIV the molecule has the C—C bond almost perpendicular to the surface plane and the interaction takes place through the oxygen atom of the carbonyl and hydroxyl groups, respectively. Conversely, the molecular symmetry plane lies (almost) parallel to that of the surface in both ad-structures cV and cVI. The intramolecular hydrogen bond has been retained in cVI, while in cV it has been removed in order to favor the formation of an intermolecular hydrogen bond with the surface. Finally, cVII and cVIII have been designed to be dissociative adsorptions, with the O and the H atoms of the hydroxyl function bonded respectively to an under-coordinated Ti and O of the anatase (1 0 1) surface, the only substantial difference being the location of the dissociated proton.

Based on the structures obtained from these explanatory runs, computations have been refined using a thicker slab of 12 atomic layers. The resulting geometries are reported in Figure 2, and Table 2 lists the principal geometrical parameters for each distinct adsorption configuration. Adsorption energies and harmonic spectroscopic data (frequencies and intensities) are collected in Tables 3 and 4, respectively. It should be noted that cII and cIV have converged to the same output structure, hence results are reported only for the former.

Adsorption geometry and energetic. Adsorption configurations cI and cIII are quite similar for what concerns bond lengths, but there are differences up to about 3° in certain valence angle and of 15° in the dihedral angle $\delta(H_1O_1C_1O_2)$. As evident from Figure 2 both feature the GA molecule non-dissociatively anchored to the surface through the interaction of the carbonyl oxygen with a Ti atom complemented by the H-bond between the hydroxylic proton and a two-fold coordinated oxygen. In both these structures, the coplanarity of $(H_1O_1C_1O_2)$ atoms is lost, with the molecular skeleton more tilted in cIII. The larger molecular distortion is compensated by a more stronger interaction with the surface, as highlighted by the lower (signed) binding energy of cIII (–18.2 kcal mol^{-1}) than cI (–15.9 kcal mol^{-1}). The most important structural deviations from gas phase GA involve the C_1—O_1 bond length that decreases by 0.02 Å in both cI and cIII and the lengthening of the O_1—H_1 bond by nearly the same amount, because of the H-bond with the surface. Also the C_1—C_2 and C_2=O_2 bonds are affected by the adsorption interaction, the former decreases and the latter increases by about 0.01 Å.

In adsorption structure cII, the molecule interacts with the surface by means of the oxygen of the hydroxyl group anchored to a five-fold coordinated Ti ion. GA undergoes a small deviation from the planarity, bond lengths C_1—O_1 and O_1—H_1 experience an elongation of c.a. 0.02 Å and 0.01 Å while C_1—H_2 shortens by 0.01 Å. Among valence angles, the most important changes are displayed by $\angle(H_1O_1C_1)$ and $\angle(C_2C_1O_1)$: the former spreads up by about 3° whereas the latter becomes tighter by c.a. 2°.

Interestingly, cV gives rise to a dissociative adsorption with the formation of a strained epoxydic ring: the hydroxyl group dissociates with the H atom transferred to a two-fold coordinated oxygen of the surface. Meanwhile, the carbonylic oxygen forms a covalent bond with a Ti ion, thus turning the C_2=O_2 double bond into a single bond, as confirmed by its elongation by 0.14 Å. The excessive electron density on the O_1 atom is then shared with the C_2 carbon to restore its tetra-valence, with the consequent formation of a three membered ring, characterized by the shortening of the C_1—C_2 distance (0.04 Å) and the lengthening of the C_1—O_1 bond (0.06 Å). The modest stability of the strained ring is reflected into an adsorption energy of only –3.1 kcal mol^{-1}.

Isomer cVI is also characterized by severe structural modifications, mainly caused by the interaction of the carbonyl oxygen with a fivefold-coordinated Ti ion, which turns the double bond into a single one. This main interaction is supplemented by an H-bond between the hydroxyl and a superficial oxygen, causing a lengthening of both O_1—H_1 and C_1—O_1. In order to favor these two interaction sites, the C_1—C_2 bond length increases by 0.03 Å. The $\angle(H_4C_2O_2)$ angle highlights the tendency of the C_2 carbon to move from sp^2 to sp^3 hybridization and all bond angles show important variations. Despite the relevant geometrical distortion, this ad-structure has an adsorption energy of –12.5 kcal mol^{-1}.

In the dissociative adsorption configuration cVII, the anchoring takes place only through the hydroxyl oxygen that forms a bond with a fivefold-coordinated Ti ion, while the proton bonds to a surface oxygen. The new O_1—Ti bond in turn causes a reinforcement of the C_1—O_1 bond which shortens by 0.03 Å; other significant changes on bond lengths involve $C_2=O_2$ and C_1—H_3. This interaction model is predicted to have an adsorption energy of –14.4 kcal mol^{-1}.

As a final comment, it is worth noticing that inspection of Table 3 reveals that the energetic of the adsorption of GA on TiO_2 anatase (1 0 1) is dispersion dominated. Indeed, the adsorption energy would be much weaker if not corrected for dispersion correlations. The two most stable configurations, cII and cIII, would be weaker by about 11 kcal mol^{-1} and in cV and cVI the GA molecule would be even unbound. Long-range correlations provide a stabilization in the range 10 – 14 kcal mol^{-1}, showing, one more time, the importance of London forces in ruling molecular adsorption on surfaces.[63,71-73]

Vibrational properties of ad-structures. In order to keep the discussion as short as possible, the attention is here focused on the main features concerning the vibrational frequencies of adsorbed GA with respect to the gas-phase molecule and in particular those above 1000 cm^{-1}, because these are compared to laboratory DRIFT spectra in a subsequent step, to gain some experimental evidence about the adsorption interaction. Particular attention will be given to the frequencies of the two functional groups of the molecule, i.e. the hydroxyl and carbonyl stretching frequencies. The vibrational frequencies of adsorbed GA, computed at harmonic level, are collected in Table 4 for the different adsorption configurations simulated.

As anticipated in the previous Section, cI and cIII share common structural features that are mirrored in the variation of GA vibrational frequencies caused by adsorption. For both of them, the main frequency shift involves the O—H stretching frequency which moves from 3725 cm^{-1} of the gas-phase molecule to 3345 and 3443 cm^{-1} for cI and cIII, respectively. In these two isomers the adsorption interaction takes also place through the carbonyl functionality, and hence the C=O stretching frequency undergoes a red shift of about 30 and 50 cm^{-1} in cI and cIII ad-structures, respectively. As evident from Table 4, other important frequency shifts concern ω_8, ω_2, ω_5, ω_9 (blue shift) and ω_3 (red shift). The main differences between the vibrational properties of cI and cIII actually manifest in the normal modes originally belonging to the A'' symmetry species of the isolated molecule. In fact, ω_{13} (CH_2 asymmetric stretching) and ω_{15} (out of plane O=C—C—O bend) are red shifted by c.a. 20 cm^{-1} in cI, whereas they remain almost unchanged in cIII.

According to the adsorption configuration cII, GA is engaged in the interaction with the surface through the H_2COH portion of the molecule and this is reflected in the frequencies of the O—H stretching and CH_2 asymmetric stretching that move by about 100 cm^{-1} in opposite directions. While the ω_1 normal mode is red shifted, as a consequence of the hydrogen bond with the anatase (1 0 1) surface, the CH_2 asymmetric stretching experiences a blue shift because the linkage to the substrate breaks the symmetry of GA and hence this normal mode does no longer correlate with that of the free molecule. The other variations in the wavenumbers of the GA fundamental vibrations are of smaller magnitude, anyway it should be noted that the C=O stretching shows a blue shift of 17 cm^{-1}.

The formation of the strained epoxydic ring in cV causes the majority of normal modes to move more than 100 cm^{-1} compared to isolated GA, as a direct consequence of the mutated chemical nature of the adsorbate. The hugest variations are the red shifts of the ω_1 and ω_4 stretching frequencies by 403 and 314 cm^{-1}: as a matter of fact these normal modes are no longer related to those of GA. The former now describes the stretching frequency of a surface OH group and the original C=O double bond turns into a single bond with a consequent weakening of its force constant.

In cVI, the most important changes involve the ω_1 and ω_4 vibrations, both of which undergo notable red shifts of about 190 and 340 cm^{-1}, respectively. These were expected, as both the O—H and C=O functional groups are directly engaged in the interaction with anatase (1 0 1). The fact that ω_4 shifts to 1480 cm^{-1} highlights a reduction in the C=O bond order stemming from the formation of two new bonds between the carbon and oxygen atoms of GA with the oxygen and titanium ions of the surface, respectively. The shift of ω_1 emphasizes the formation of a hydrogen bond between the molecule and the surface. Furthermore, the CH_2 asymmetric stretching (ω_2) and the aldehydic CH stretching (ω_3), are blue shifted by about 100 and 75 cm^{-1}, due to the shortening of the corresponding bond lengths. The CH_2 group is also involved in the normal modes ω_6 and ω_{13} that undergo a shift of about 40 cm^{-1} in opposite directions.

Finally, in cVII the foremost frequency shift interests the C—O stretching that moves from 1142 cm^{-1} in free GA to 867 cm^{-1} in the adsorbed molecule. Despite the shortening of the C—O bond length, that would suggest blue frequency shift, the predicted red shift is likely due to an increase of the reduced mass moving during the vibrational motion. For the same reason also the normal modes ω_3, ω_6, ω_8 and ω_{13} are calculated to be red shifted by about 50 - 60 cm^{-1}, while the red shift of the C=O stretching is coherent with the lengthening of this bond. Lastly, it should be noted that the ω_1 frequency calculated at 3690 cm^{-1} obviously refers to the newly formed hydroxyl group on the anatase (1 0 1) surface.

Drift experiments. Differential DRIFT spectra of GA adsorbed on titanium dioxide are presented in Figure 3, where the relevant absorptions are also labeled. Differential spectra have been obtained by a least squares procedure that minimizes the differences between the spectra of adsorbed and free GA, thus reducing the possibility of artifacts in the observed bands appearing in the differential spectra. By comparing the absorptions measured for the adsorbed molecule, with those of the gas phase species, the most important experimental evidences of the adsorption process are the red shift of both ν_1 and ν_4 bands, corresponding to the O—H and C=O stretching motions, respectively. According to the DRIFT spectra of GA anchored on the solid substrate, the ν_1 fundamental (3549.4 cm^{-1} in the isolated GA) is shifted to 3127 cm^{-1} and the ν_4 band (1754.1 cm^{-1} for GA in the gas phase), is red shifted by about 38 cm^{-1}.

By complementing these observations with the results of the quantum chemical simulations it is possible to get more insights into the adsorption configurations of GA on TiO_2. The observed spectrum is actually the Boltzmann's average of the possible different adsorption configurations coexisting on the surface, thus a rigorous way to proceed would be to simulate the spectrum as the average of the spectra corresponding to the different ad-structures, each weighted according to the relative energies.[73] However, in order to obtain results consistent with experiments, Gibbs free energies should be used in place of electronic energies. Under this point of view, computational protocols able of delivering chemical accuracy have been developed and applied to simulate adsorption isotherms.[80-82] This is out of the aim of the present work, being this the first investigation about the interaction of GA with TiO_2. Hence, the consistency between theory and experimental is here addressed on a per-structure basis. Ad-structures cV and cVI should be discarded as more likely adsorption configurations, in fact they lack of the carbonyl group whose stretching is, however, present in the measured spectra. Despite the strongest adsorption energy computed for cII, a blue shift of about 20 cm^{-1} has been theoretically predicted for the ν_4 band, at variance with the red shift of ~40 cm^{-1} measured experimentally. As to the strongest interaction energy of –19.7 kcal mol^{-1}, it should be noted that this conformer is more stable than cIII by only 1.5 kcal mol^{-1}, and hence thermal contributions could easily switch the energy order of these two adsorption configurations. Configuration cVII appears of little significance for interpreting the observed spectra, because even though the red shift of both the O—H and C=O stretching frequencies is correctly reproduced by theoretical computations the extent of the former appears very small compared to that measured experimentally. Therefore, cI and cIII are the adsorption configurations that most closely match with the experimental outcomes. In fact, upon adsorption, both the stretching frequencies ν_1 and ν_4 associated with the two functional groups of the molecule undergo a red shift. As already pointed out, cI and cIII describe very similar adsorption configurations and hence they are both likely to contribute to the measured DRIFT spectra. Yet, from a theoretical point of view, cIII is predicted more stable and hence it represents the most likely adsorption configuration of the GA molecule adsorbed on the surface of anatase (1 0 1).

A tentative assignment of the observed experimental absorptions of GA anchored on the TiO_2 surface based on the theoretical simulations performed for models cI and cIII is reported in Table 5. In addition to the harmonic vibrational frequencies, this table also lists those obtained by scaling the harmonic wavenumbers in order to account some anharmonicity. Its inclusion is fundamental for the comparison between theory and experiment as vibrations measured experimentally are intrinsically anharmonic. In general, literature proposes several sets of scaling factors tailored for a specific level of theory, but it is not uncommon that they badly reproduces anharmonic shifts, in particular when small (or even positive) anharmonic constants are present. For this reason, in this work the harmonic vibrational frequencies of the adsorbed molecule have been scaled by using “ad hoc” scaling factors, obtained by requiring that the scaled vibrational frequencies computed for the free molecule reproduce the experimental ones.[73] As it can be observed from the mean deviations (MD) and mean absolute deviations (MADs) reported in the table, scaled frequencies are, by far, in better agreement with the experimental frequencies (MADs are more than halved) underlying the importance of including anharmonic effects. In general, a satisfactory agreement can be reported between computed and observed wavenumbers for both adsorption configurations cI and cIII, the deviation being usually smaller than 40 cm^{-1}. It can be noted that no experimental evidence has been gained for the ν_2 and ν_{13} vibrations. Clearly, it is possible that these two absorptions have an intensity too weak to be observed. In this respect it should be pointed out that the theoretical intensity reported in Table 4 should be taken with care, as it has been obtained within the double-harmonic approximation and inclusion of electrical anharmonicity may significantly reduce the absorption cross section obtained harmonically. In spite of these considerations, scaled theoretical wavenumbers reproduce the experimental ones with a MAD of about 30 cm^{-1}, an accuracy comparable to that of full anharmonic B3LYP calculations for the gas-phase molecule. Furthermore theoretical and observed vibrational wavenumbers result linearly correlated and they can be fitted to straight lines ($R^2 = 0.999$) passing though the origin with a slope 1.008 (± 0.005) and 1.019 (± 0.007) for cI and cIII, respectively (see also Figure S.2 of Supporting Information). Therefore, the results obtained for GA anchored on the surface of TiO_2 can be considered to provide a realistic description of the physical-chemistry of the adsorption process. Building on this, a number of further developments can be thought in order to refine the theoretical model. The energetics can be computed by including thermal effects and lateral interactions, while anharmonic contributions to vibrational frequencies could be included quantum mechanically e.g. by using a small, but physically representative, molecular complex.[83] Furthermore, since in the present work GA is part of the repeating pattern, co-adsorption of molecules with different arrangements can be simulated and it can also be of some interest to study the effects of water co-adsorption on the molecule-surface interaction. The latter should be complemented by new experiments performed to allow H_2O adsorption.

Conclusions

Although GA is technically not 'the first interstellar sugar,' as it has been labelled[1,6], it is the simplest molecule containing two different functional groups, an hydroxyl and a carbonyl, and hence of chemical formula $(H_2CO)_{n=2}$. The discovery of GA in interstellar space, and the fact that it is actively involved in the formose reaction leading to ribose, clearly comes with fascinating clues about the origin of life in the Universe as well as in a primeval Earth. Under this point of view, the catalytic role of a mineral surface in its chemistry needs to be explored and is done so in this work.

In this work, the adsorption interaction of GA on TiO_2 has been deeply investigated by means of quantum chemical simulations, being this the first essential step disclosing the reactive pathway mediated by the surface. Quantum mechanical calculations have been carried out at DFT-B3LYP level by considering a 12-layer slab cut from the anatase bulk along the (1 0 1) plane. By pursuing the periodic approach, the structural, energetic and vibrational properties of GA have been computed for six different adsorption configurations. The outcomes show that the interaction of GA with the substrate is mainly dispersion dominated and the structures in which the molecule is more strongly bound to anatase (1 0 1) are cI, cII and cIII (see Figure 2). In addition to the theoretical investigation, DRIFT spectra of GA interacting with TiO_2 have been recorded in order to gain experimental information about the adsorption process against which facing the theoretical predictions. The experimental results suggest that GA binds to the TiO_2 surface by means of either the O—H and the C=O groups as manifested by the red shift of the corresponding stretching frequencies. Comparison with theoretical predictions has suggested that the most probable adsorption mechanism of GA over the surface of TiO_2 is cIII.

Although the most stable adsorption configuration of GA over TiO_2 is represented by a non-dissociative anchoring, quantum chemical simulations have shown that the interaction of GA with the surface of anatase (1 0 1) may potentially lead to a significant activation of the C=O bond through its lengthening or even the formation of reactive species, like strained epoxydic ring. Under this point of view, these outcomes suggest that mineral catalysis is one of the possible important processes disclosing the reaction pathway for the evolution of the GA toward more complex prebiotic molecules.

Supporting Information

Figure S.1, Adsorption configurations devised for the possible interactions of GA with the TiO_2 Anatase (1 0 1). Figure S.2, Linear fits of theoretical vs. experimental vibrational frequencies for GA adsorbed on TiO_2.

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Table 1. Approximate description, experimental and theoretical wavenumbers (cm^{-1}) for the vibrational normal modes of gas phase glycolaldehyde

Symmetry Species	Normal Mode	Approximate Description [a]	$\nu_{exp.}$ [a]	$\nu_{B3LYP/pc-1}$ [b]	$\nu_{M06-2X/pc-1}$	$\nu_{B2PLYP/cc-pVTZ}$
A'	ν_1	O—H stretch	3549.43	3546	3563	3545
	ν_2	CH_2 symmetric strecth	2885.02	2907	2980	2870
	ν_3	Aldehydic C—H strecth	2832.08	2801	2930	2823
	ν_4	C=O stretch	1754.14	1793	1845	1755
	ν_5	CH_2 scissor	1458.04	1426	1509	1466
	ν_6	ip CH_2 wag	1425.43	1391	1414	1405
	ν_7	ip O=C—H bend	1364.17	1361	1417	1371
	ν_8	ip C—O—H bend & C—C stretch	1275.27	1256	1332	1277
	ν_9	C—O stretch	1114.69	1117	1183	1112
	ν_{10}	C—C stretch	860.51	833	872	855
	ν_{11}	ip C—C=O & H—O—C bends, out of phase	751.61	749	776	751
	ν_{12}	ip C—C—O & C—C=O bends, in phase	307.12	256	431	280
A"	ν_{13}	CH_2 asymmetric strecth	2881.07	2868	2962	2876
	ν_{14}	CH_2 twist & oop O=C—H bend	1228.95	1223	1233	1230
	ν_{15}	oop O=C—C—O	1084	1088	1095	1092
	ν_{16}	oop aldehydic C—C—H wag	700.30	745	696	719
	ν_{17}	oop C—O—H & C—C=O wags out of phase	359.57	411	571	363
	ν_{18}	oop C—O—H & C—C=O wags in phase	207.19	260	364	216
MD [c]				0	–63	2
MAD [d]				24	65	8

[a] From Ref. 20; oop and ip indicate in-plane and out-of-plane, respectively.

[b] Crystal14 harmonic frequencies corrected for anharmonic effects through cubic and quartic semidiagonal force constants evaluated by Gaussian16.

[c] Mean deviation (cm^{-1}).

[d] Mean absolute deviation (cm^{-1}).

Table 2. Main structural parameters of GA in the gas phase and adsorbed on TiO_2 anatase (1 0 1) computed at B3LYP/pc-1 level [a]

	Gas phase GA	GA @ TiO_2 anatase (1 0 1)					
		cI	cII	cIII	cV	cVI	cVII
C_1—C_2	1.508	1.499	1.505	1.497	1.468	1.542	1.504
C_1—O_1	1.401	1.382	1.422	1.382	1.461	1.411	1.372
C_2=O_2	1.211	1.220	1.208	1.223	1.351	1.403	1.221
C_1—H_2	1.108	1.104	1.098	1.105	1.094	1.103	1.109
C_1—H_3	1.108	1.117	1.103	1.116	1.094	1.098	1.118
C_2—H_4	1.115	1.111	1.114	1.110	1.094	1.103	1.113
O_1—H_1	0.976	0.995	0.983	0.990	1.748	0.984	2.837
$\angle(C_2C_1O_1)$	113.1	116.9	110.9	115.9	59.3	115.1	117.6
$\angle(C_1C_2O_2)$	122.2	125.8	122.4	122.1	122.0	116.6	128.2
$\angle(C_1C_2H_4)$	116.2	116.2	115.4	117.8	120.6	110.2	113.8
$\angle(H_4C_2O_2)$	121.7	117.9	122.2	119.8	112.9	109.4	118.0
$\angle(H_1O_1C_1)$	106.7	108.6	110.1	108.2	105.7	110.2	111.7
$\angle(H_2C_1H_3)$	106.2	105.2	106.9	105.0	116.3	108.3	106.1
$\delta(H_1O_1C_1O_2)$ [b]	0.0	47.1	19.4	61.9	65.7	35.1	57.9
$H_1\cdots O(2c)$		1.619	2.892	1.726	0.990	1.775	0.972
$H_1\cdots O(2c)$			2.936			2.864	
$O_2\cdots Ti(5c)$		2.181		2.178	1.839	1.866	2.206
$H_4\cdots O(2c)$				2.838		2.062	
$O_1\cdots O(2c)$		2.599		2.710			
$O_2\cdots O(2c)$		2.767		2.813	2.570	2.157	2.654
$O_1\cdots Ti(5c)$			2.184				1.891
$O_1\cdots O(2c)$			2.755		2.645		2.677
$H_2\cdots O(2c)$			2.675		2.285		
$H_3\cdots O(2c)$			2.833				2.482
$C_2\cdots O(2c)$						1.422	
$C_1\cdots O(2c)$						2.453	
$C_2\cdots Ti(5c)$						2.544	

[a] Bond lengths and angles in Å and deg, respectively. O(2c) and Ti(5c) indicate bi- and penta-coordinated oxygen and titanium atoms of the surface, respectively.

[b] δ denotes the dihedral angle defined by the atoms given within parentheses.

Table 3. Interaction energies (kcal mol^{-1}) for the adsorption of GA on TiO_2 anatase (1 0 1) according to different configurations

Adsorption configuration	ΔE B3LYP/VTZ [a]	BSSE B3LYP/VTZ	E_{disp} B3LYP-D2/VTZ	$\Delta E_{(CP)}$ B3LYP/VTZ [b]	$\Delta E_{(CP)}^{disp}$ B3LYP-D2/VT [c]
cI	-11.1	9.9	-19.5	-6.1	-15.9
cII	-13.7	10.2	-22.1	-8.6	-19.7
cIII	-12.4	11.0	-22.7	-6.9	-18.2
cV	1.1	15.3	-23.7	8.8	-3.1
cVI	-7.5	16.7	-27.4	1.2	-12.5
cVII	-9.5	18.3	-28.2	-0.3	-14.4

[a] Interaction energy at B3LYP/cc-pVTZ(GA)/pob-TZVP(TiO_2) level.

[b] Counterpoise corrected interaction energy at B3LYP/cc-pVTZ(GA)/pob-TZVP(TiO_2) level.

[c] Counterpoise- and dispersion- corrected interaction energy at B3LYP-D2/cc-pVTZ(GA)/pob-TZVP(TiO_2) level.

Table 4. Harmonic vibrational wavenumbers (cm^{-1}) and intensities (km mol^{-1}) for GA free and adsorbed on TiO_2 anatase (1 0 1) obtained at B3LYP/pc-1 level.

Normal Mode	ω_{GA}	I_{GA}	ω_{cI}	I_{cI}	ω_{cII}	I_{cII}	ω_{cIII}	I_{cIII}	ω_{cV}	I_{cV}	ω_{cVI}	I_{cVI}	ω_{cVII}	I_{cVII}
ω_1	3725	111.7	3345	765.2	3620	223.1	3443	607.4	3322	1133.0	3534	577.1	3690	674.6
ω_2	3024	90.7	3073	32.7	3053	14.6	3074	31.1	3215	72.3	3120	103.2	3007	85.8
ω_3	2953	100.3	2901	33.9	2970	40.8	2913	35.2	3115	12.2	3027	54.9	2896	91.1
ω_4	1818	54.5	1790	253.3	1835	194.4	1771	314.7	1504	50.1	1480	38.4	1776	402.6
ω_5	1474	40.8	1512	60.3	1469	43.8	1515	51.0	1407	73.7	1471	25.4	1427	42.0
ω_6	1435	53.7	1443	14.8	1421	60.7	1441	19.2	1311	204.1	1391	5.5	1378	51.9
ω_7	1389	29.1	1410	26.5	1391	32.5	1402	11.5	1226	155.3	1389	55.8	1411	129.9
ω_8	1288	43.9	1385	19.9	1305	45.7	1378	83.7	1167	18.1	1292	19.5	1225	199.1
ω_9	1142	118.4	1182	69.9	1134	45.8	1177	84.4	1121	112.1	1138	92.5	867	150.1
ω_{10}	855	74.3	875	83.7	869	75.9	865	32.5	1004	53.9	1010	25.1	863	128.9
ω_{11}	764	6.7	845	55.9	778	43.5	786	45.1	872	172.5	884	87.5	818	112.1
ω_{12}	272	37.0	313	13.1	402	13.4	367	22.7	566	18.6	662	90.0	440	119.2
ω_{13}	3018	90.5	2999	60.4	3124	41.1	3020	47.1	3161	12.4	3061	65.5	2953	25.6
ω_{14}	1252	0.1	1246	17.0	1229	37.9	1253	29.8	1202	47.3	1257	24.0	1258	24.9
ω_{15}	1110	0.1	1088	12.1	1092	31.9	1104	20.8	1097	24.8	1096	155.5	1097	17.7
ω_{16}	759	1.2	802	41.4	734	2.8	767	126.6	832	102.4	805	69.3	659	10.2
ω_{17}	426	105.4	647	4.5	530	154.4	726	50.2	768	100.8	725	198.8	508	148.7
ω_{18}	249	11.2	286	14.3	256	0.7	270	17.3	471	21.3	540	31.4	279	48.4

Table 5. Comparison between experimental and theoretical vibrational wavenumbers (cm^{-1}) of GA adsorbed on TiO_2.

Normal Mode	ω_{cI}[a]	ν_{cI}[b]	ω_{cIII}[a]	ν_{cIII}[b]	Exp
ν_1	3345	3188	3443	3281	3127
ν_2	3073	2931	3074	2932	- [c]
ν_3	2901	2782	2913	2794	2798
ν_4	1790	1727	1771	1709	1716
ν_5	1512	1496	1515	1499	1465
ν_6	1443	1433	1441	1431	1402
ν_8	1385	1372	1378	1364	1333
ν_9	1182	1154	1177	1149	1171 [d] /1131[e]
ν_{13}	2999	2862	3020	2882	- [c]
ν_{14}	1246	1223	1253	1229	1228
ν_{15}	1088	1063	1104	1078	1088
MD [f]	-63	12	-79	-27	
MAD [g]	63	26	79	32	
R^2 [h]		0.9998		0.9995	

[a] Harmonic wavenumbers.

[b] Scaled wavenumbers. For the scaling procedure, see text.

[c] Not assigned because of band overlaps

[d] Assigned to cI.

[e] Assigned to cIII.

[f] Mean deviation respect to experimental data (cm^{-1}).

[g] Mean absolute deviation respect to experimental data (cm^{-1}).

[h] R^2 for the linear fit of ν^{theo} vs. ν^{exp}.

Figure & Figure Captions

Figure 1. Structure and atom labeling of the cis-cis glycolaldehyde conformer.

Figure 2. Adsorption configurations of GA interacting with the TiO_2 anatase (1 0 1) surface. The simulation cell is replicated twice in the **a** and **b** directions for better visualization.

Figure 3. Differential DRIFT spectra of GA adsorbed on TiO_2 between 1000 and 4000 cm^{-1} at different exposure times: 0 s, 180 s, 360 s, 540 s, 720 s from top to bottom. The solid substrate is composed of 75% TiO_2 nano-powder and 25% KBr. Relevant absorptions wavenumbers are indicated. The asterisk denotes a possible artifact due to spectra subtraction.

TOC Graphic