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Article

Conformer-Selective Adsorption of 1-Propanol on the Ag(111) Surface

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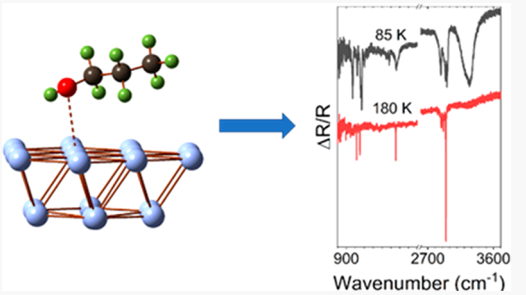
ABSTRACT: Reflection absorption infrared spectra (RAIRS) were simulated with density functional theory calculations for five different rotational conformers of 1-propanol on the Ag(111) surface for comparison to the corresponding experimental spectra. The experimental RAIR spectra were obtained by adsorbing multilayers of 1-propanol at 90 K and then annealing the surface to 180 K to desorb the multilayer and produce the most stable 1-propanol monolayer structure on Ag(111). The multilayer spectrum features a broad O−H stretch characteristic of hydrogen bonding between the molecules as well as broad and complex peaks in the C−H stretch and C−H deformation regions. After annealing to 180 K, the O−H stretch peak disappears, and the remaining peaks are unusually sharp. Comparison of the experimental and simulated spectra indicates that 1-propanol adsorbs as only one of the five conformers.



INTRODUCTION

Knowledge of the structure of molecules adsorbed on metal surfaces is crucial for understanding the mechanisms of surface chemical reactions. For small molecules that exist in only one structural form in the gas phase, specifying their structure on surfaces usually consists of identifying the adsorption site and orientation of one or two molecular axes with respect to the surface normal. For example, CO usually adsorbs at either atop, twofold bridge, or threefold hollow sites with the CO axis perpendicular to the surface[1] and ethylene can adsorb in a π-bonded form in which the planar molecule lies flat on the surface, or in a di-σ form with the CC axis parallel to the surface, but the CH_2 planes tilted away from the surface.[2] The situation can be more complex for polyatomic molecules that can exist as multiple rotational conformers due to low or nonexistent barriers for rotation about single bonds. For 1-propanol, $CH_3CH_2CH_2OH$, low rotational barriers about the two C−C bonds and the C−O bond lead to five unique rotational conformers with very similar energies such that at room temperature the gas phase consists of an equilibrium mixture of conformers. Here we use reflection absorption infrared spectroscopy (RAIRS) to show through a comparison of experimental and theoretical spectra that interaction with the Ag(111) surface leads to adsorption of only one of these conformers. This is an aspect of the surface chemistry of 1-propanol that has not been considered in previous studies of its adsorption and reaction on metal surfaces.[3−8]

The different conformers of 1-propanol are illustrated in Figure 1 and can be understood in terms of dihedral angles between the CCC, CCO, and COH planes. Following the

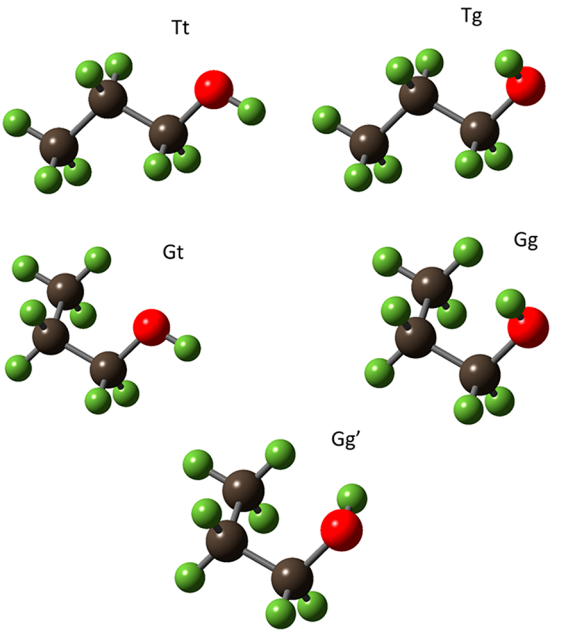


Figure 1. Five conformers of 1-propanol in the gas phase. Black: Carbon; Green: Hydrogen; Red: Oxygen.

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notation of Radom et al.,[9] we use two letters to designate the conformer. The first letter, T or G for trans or gauche, indicates the angle between the CCC and CCO planes (the CCCO dihedral angle). When the CCCO atoms are in the same plane and the CO and C−CH_3 bonds are trans, the CCCO dihedral angle is 180° and the first letter is T, whereas rotating the CCCO dihedral angle by ±120° gives conformers with a first letter of G. When the CCOH dihedral angle is 180°, the second letter is t. Thus, when the CCCOH atoms are coplanar, the conformer is Tt. From the Tt conformer, rotating the CCOH dihedral angle by either + or −120° gives the same conformer, designated Tg. However, from the Gt conformer, rotation of the CCOH angle by +120° gives Gg where the OH bond and the CH_3 group are on the opposite sides of the CCO plane, whereas rotation of the CCOH angle by −120° gives the Gg′ conformer, with the OH bond and CH_3 group on the same side of the CCO plane. This gives five distinct conformers, designated Tt, Tg, Gt, Gg, and Gg′, that have local potential energy minima as a function of the two dihedral angles. The structures of these conformers have been well described in previous publications.[9−11] The different conformers of 1-propanol have been the subject of several spectroscopic studies.[12,13]

The reaction of all five conformers of gas-phase 1-propanol with O(^{3}P) atoms was investigated computationally at a high level by Troya who found substantial differences in the reaction pathways.[11] He notes that the conformer-dependence of the reactivity is often ignored and cites several computational studies of 1-propanol interacting with surfaces including Au(111)[14] in which only the Tt conformer was considered. His calculations show that the Gt conformer is more stable than Tt by only 0.02 kcal/mol. Earlier high-level calculations also concluded that the Gt conformer is most stable.[15] Given such a small energy difference, it is quite likely that the relative stability of the conformers in the gas phase cannot be assumed to apply to the adsorbed molecule. Rather than predicting which conformer is most stable on the Ag(111) surface based on their calculated relative energies, we show that the simulated RAIR spectrum of only one conformer is a good match to the experimental spectrum. Based on this match, we conclude that 1-propanol adsorbs exclusively as the Tt conformer on Ag(111). This conformer is also calculated to be most energetically stable in the gas phase and when bonded to a Ag_{19} model of the Ag(111) surface at the level of theory we used.

COMPUTATIONAL METHODS

Density Functional Theory (DFT) calculations of the five 1-propanol conformers alone and adsorbed on a silver cluster (Ag_{19}) model of the Ag(111) surface were performed with the Gaussian 16 program.[16,17] Geometry optimization of the Ag_{19} cluster was first performed with the PBE exchange functional and LanL2DZ basis set, and then the energy of the crystal was calculated with the B3LYP exchange-correlation functional and LanL2DZ basis set. Geometry optimizations and harmonic frequency calculations of the conformers in the gas phase and on the Ag_{19} cluster were performed with the B3LYP functional and 6-31G(d,p) and 6-311++G(2d,2p) basis sets. The calculations were performed using the frozen core option for the Ag_{19} cluster when calculating the properties of the adsorbed conformers. The computations were conducted using the OPT = tight option that tightens the criteria for cutoff of forces and the step size for the convergence and INT = ultrafine option that modifies the use of two-electron integrals and their derivatives. The ultrafine option uses a pruned (99,590) grid. Pruned grids are optimized grids to reach a given level of accuracy by using a minimum number of points. To include empirical dispersion, the D3 version of Grimme's dispersion[18,19] with the original D3 damping function was added with the option EmpiricalDispersion = GD3. The adsorption energies of propanol on Ag_{19} were computed and corrected for their zero-point energies (ZPE). The change in energy upon adsorption (ΔE) was calculated using the formula:

$$\Delta E = (E_{\text{cluster}} + E_{\text{conf}}) - E_{\text{ad}}$$

where E_{ad} = energy of adsorbed molecule and cluster, E_{conf} = energy of a conformer in the gas phase, and E_{cluster} = energy of the cluster. Each energy is a negative quantity since the zero of energy is defined as the separated nuclei and electrons. Therefore, a positive ΔE corresponds to stable adsorption and the adsorbed conformer with the most positive ΔE is predicted to be the one that is most stably adsorbed.

Vibrational frequencies of the optimized structures were computed at the B3LYP/6-311++G(2d,2p) level. The absence of imaginary frequencies confirmed that the optimized structures were at energy minima. To compare to the experimentally observed frequencies, the computed frequencies were scaled by a factor of 0.965, the value appropriate for the B3LYP/6-311++G(2d,2p) level. The intensities of the peaks were taken as the square of the components of the calculated dipole moment derivatives along the surface normal. Unlike in the gas phase, only this component contributes to the intensity of a given peak in the RAIRS experiment. The simulated vibrational spectra were generated from the calculated frequencies and intensities assuming a Lorentzian line profile with a full width at half-maximum (fwhm) of 4 cm^{-1}.

EXPERIMENTAL SECTION

The experiments were performed in an ultrahigh vacuum (UHV) chamber with a base pressure of 1×10^{-10} Torr equipped for RAIRS, temperature-programmed desorption (TPD), low energy electron diffraction (LEED), and Auger electron spectroscopy (AES). A complete description of the apparatus along with the mounting and cleaning procedure of the Ag(111) crystal and additional details of the 1-propanol experiments are described elsewhere.[20,21] The RAIR spectra presented here were obtained at 1 cm^{-1} resolution with 1024 scans for an acquisition time of approximately 8 min per spectrum. In an earlier publication we presented RAIR spectra of 1-propanol obtained at a resolution of 4 cm^{-1} as a function of exposure and annealing temperature along with TPD results.[21]

RESULTS AND DISCUSSION

In Table 1, the calculated energies relative to the energy of the most stable conformer from our calculations and those of Troya[11] are compared for the five conformers of gas phase 1-propanol. Troya carried out geometry optimizations using Møller−Plesset perturbation theory through second order with a correlation-consistent polarized valence triple-ζ basis set (MP2/cc-pVTZ).[11] He further refined the energies with the coupled cluster method with singles, doubles, and triples (CCSDT) using a cc-VNZ, N = double, triple, quadruple, basis

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Table 1. Relative Energies in kcal/mol for the Five Rotational Conformers for Gas-Phase 1-Propanol from Our Calculations and from Those of Troya[11]

Conformer	B3LYP/ 6-311++G(2d,2p)	CCSD(T)/CBS//MP2/cc-pVTZ (Troya)
Gt	0.08	0
Tt	0	0.02
Tg	0.06	0.07
Gg	0.21	0.18
Gg′	0.28	0.17

set. The results were extrapolated to the complete basis set limit.[11] While Troya's results are undoubtedly more accurate than our DFT calculations, it was not feasible for us to carry out such high-level calculations for 1-propanol bonded to a Ag_{19} cluster. The comparison in Table 1 indicates that although our DFT calculations yield similar energies to those of Troya, the ordering is somewhat different with his calculations indicating that the Gt conformer is more stable than Tt by 0.02 kcal/mol, whereas our calculations indicate that Tt is more stable than Gt by 0.08 kcal/mol, which we calculate to be slightly less stable than the Tg conformer. Our calculations agree with Troya's results that the Gg and Gg′ conformers are less stable than the other three. An important conclusion from either set of calculated energies is that, at room temperature (298 K) where kT = 0.59 kcal/mol, the 1-propanol vapor that was exposed to the surface should have been an equilibrium mixture of the different conformers, and kT even at 180 K is still higher than the energy difference between conformers so that a mixture of conformers would be present, unless the interaction with the surface favors one or more of the possible conformers.

For the conformers interacting with the Ag_{19} cluster, geometry optimization indicates that all five conformers bond to an atop site as illustrated in Figure 2. Bonding through the O atom to an atop site was also reported in a DFT study of 1-propanol on Au(111).[14] The adsorption energies and adsorption energies relative to the most strongly bound Tt conformer are given in Table 2 for two basis sets. The Tt conformer is calculated to be the most stably adsorbed conformer for both basis sets, while the Gg′ and Gg conformers have the second and third highest adsorption energies. However, the fourth and fifth largest adsorption energies are different for the two basis sets. The calculated result that the Gg′ conformer has the second largest adsorption energy contrasts with the gas phase calculation where it was found to be the least stable conformer. A comparison of the results in Tables 1 and 2 shows that the differences in adsorption energies of the different conformers are considerably greater than their relative energies in the gas phase. This illustrates that interaction with the surface must be included to assess which conformer is most stably adsorbed. Because of this greater difference, it is plausible that interaction with the surface will strongly favor one conformer over the other, even if several conformers can coexist in the gas phase.

The differences in the calculated adsorption energies are small and are likely less than the accuracy of the calculation. For this reason, we have chosen to focus on a comparison between experimental and simulated IR spectra to identify the conformation of 1-propanol on Ag(111). Michniewicz et al. presented simulated IR spectra of the five conformers of gas phase 1-propanol based on DFT calculations, which showed

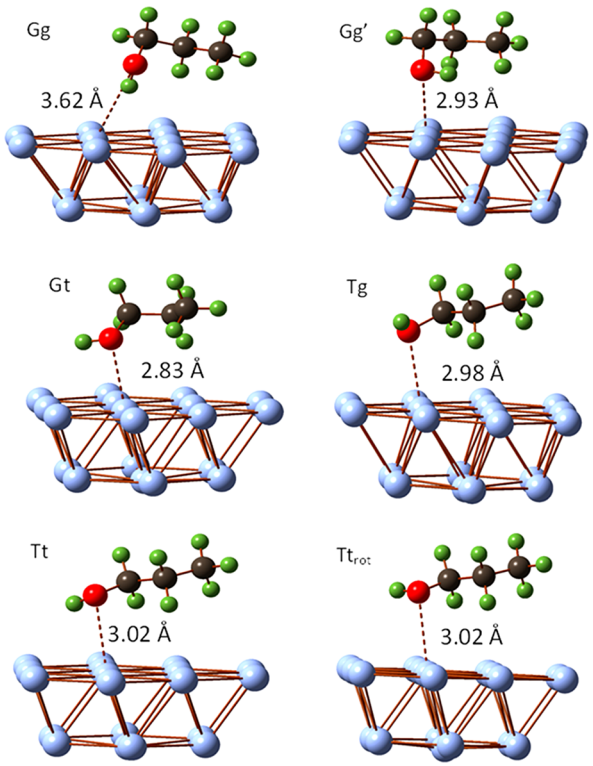

Figure 2. Geometry-optimized structures of the five 1-propanol conformers bound to a Ag_{19} model of the Ag(111) surface. Tt_{rot} refers to the Tt conformer in which only the O−H bond was rotated to make is more nearly parallel to the surface.

Table 2. Calculated Energies in kcal/mol of the Five 1-Proponal Conformers Bonded to a Ag_{19} Cluster Model of the Ag(111) Surface and Adsorption Energies (in Parentheses) Relative to the Adsorbed Tt Conformer[a]

Conformer on Silver cluster	B3LYP/ 6-31G(d,p)	B3LYP/ 6-311++G(2d,2p)
Ag_{19}-Gg	17.92 (0.90)	16.60 (0.59)
Ag_{19}-Gg′	18.19 (0.64)	16.75 (0.44)
Ag_{19}-Gt	17.80 (1.03)	16.24 (0.95)
Ag_{19}-Tt	18.83 (0)	17.19 (0)
Ag_{19}-Tg	17.70 (1.13)	16.56 (0.63)
Ag_{19}-Tt_{rot}		16.55 (0.64)

[a]The latter are taken as positive values to facilitate comparison with the relative energies in Table 1. Also listed are results for Tt_{rot}, which is the Tt conformer with the O−H bond rotated towards the surface.

that each conformer has a distinctly different spectrum.[12] We have reproduced their results and present our simulated spectra for the five gas-phase conformers in the Supporting Information. Because the selection rule for RAIRS allows observation only of modes with a component along the surface normal, fewer peaks are predicted for a molecule adsorbed with a definite orientation. This will lead to even greater differences in the spectra of the different conformers on a surface than in the gas phase. In this sense, for a particular conformer the most pertinent role of the surface is to fix the orientation of the molecule. In fact, simulated spectra for a gas phase conformer of a specific orientation in space would likely give qualitatively similar results as simulated spectra for the adsorbed molecule. In the Supporting Information, we provide tables of frequencies and their assignments for the five conformers

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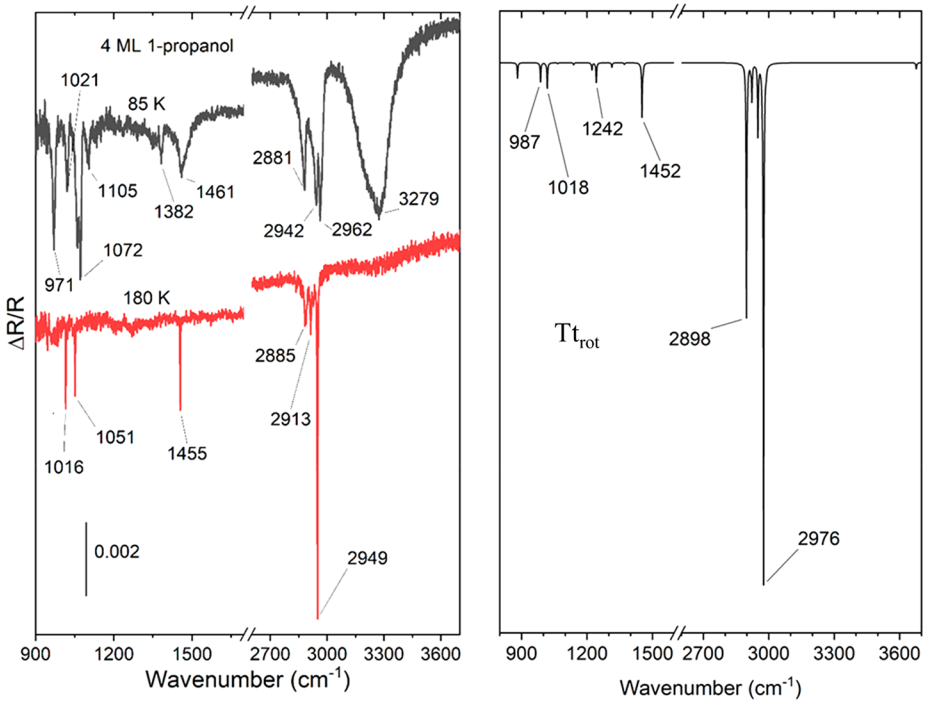

Figure 3. (Left) Experimental RAIR spectra at a resolution of 1 cm^{-1} of 4 ML of 1-propanol adsorbed on Ag(111) at 85 K (black) and after the surface was annealed to 180 K for 1 min and recooled to 85 K (red). (Right) Simulated RAIR spectrum of the Tt conformer with the OH bond rotated slightly to make it nearly parallel to the (111) face of the Ag_{19} cluster. The rotated Tt conformer is designated as Tt_{rot}.

both bonded to the Ag_{19} cluster and in the gas phase. The interaction with the surface shifts the frequencies of most modes by no more than a few cm^{-1}, supporting the idea that bonding to the surface has little effect on the internal bonding within the 1-propanol molecule. In particular, there is generally a greater variation in frequencies among the conformers than there is between the frequencies for a given conformer in the gas phase versus bonded to the surface. For this reason, the exact model used to represent the surface is of secondary importance. For example, we showed that experimental RAIR spectra of three different aminocarbyne (RR′NC, R, R′ = H or CH_3) species were equally well matched by simulated spectra from DFT calculations using either Pt_4 or Pt_9 cluster models of the Pt(111) surface.[22] Unlike the aminocarbyne molecules that strongly chemisorb on the Pt(111) surface, 1-propanol is only weakly adsorbed on the Ag(111) surface. Therefore, the simulated spectra are unlikely to depend on the exact model used to represent the surface, whether a small Ag cluster or a slab with two-dimensional periodicity.

Figure 3 shows a comparison of experimental spectra of propanol and simulated spectra for the Tt conformer, modified as described below, which is the one that best matched the experimental spectrum. After adsorption at 85 K, several broad and poorly resolved peaks are observed in the experimental spectrum in Figure 3. The red shift of the intense and broad O−H stretch at 3279 cm^{-1} from its gas phase value[23] of 3687 cm^{-1} is indicative of hydrogen bonding between the molecules. Based on TPD peak areas, the multilayer coverage after adsorption at 85 K was estimated as 4 monolayers (ML). The multiple peaks present in the multilayer spectra is likely due to the presence of multiple conformers as well as an ill-defined mix of different orientations of those conformers. Generally, IR spectra of monolayers are similar to those of the molecular solid, but we are not aware of any published IR spectra of solid propanol. However, Fukushima and Zwolinski[23] performed a detailed analysis of all 30 normal modes of 1-propanol in the gas and liquid phases and our assignments in the Supporting Information follow theirs. The peak for the multilayer at 971 cm^{-1} in Figure 3 is for the C−O stretch, and the fact that it disappears upon annealing along with the O−H stretch suggests that after annealing the molecule is oriented with both the CO and OH bonds nearly parallel to the surface.

The TPD results indicated that annealing to 180 K should desorb the multilayer, leaving first layer 1-propanol molecules behind.[21] Although it is difficult to know the absolute coverage, where one monolayer (ML) would be one molecule per surface Ag atom, the saturation coverage of small molecules such as this is generally in the range 0.25 to 0.50 ML. After annealing, the spectrum features fewer and sharper peaks, with unusually small intrinsic full width at half maxima (fwhm) of 1.1, 2.1, 1.6, and 4.0 cm^{-1} for the peaks at 1016, 1051, 1435, and 2948 cm^{-1}, respectively. The intrinsic fwhm values were estimated based on the assumption that the squares of the intrinsic fwhm and the instrumental resolution of 1 cm^{-1} add to give the square of the measured fwhm. Annealing to 180 K also eliminated the O−H stretch peak, an important characteristic of the adsorbed molecule that we sought to replicate in the simulated spectra. The remarkably simple spectrum obtained after annealing to 180 K is in sharp contrast to what would be expected for an equimolar mixture of all conformers. This is because the difference in calculated frequencies for a given mode of the different conformers is generally greater than the experimental peak widths. In Figure S9 we present a superposition of simulated spectra for the five gas-phase conformers. The large number of distinct peaks is in sharp contrast to the experimental spectrum. It is this contrast that strongly suggests that, after annealing, 1-propanol adsorbs as a single conformer of definite orientation on Ag(111).

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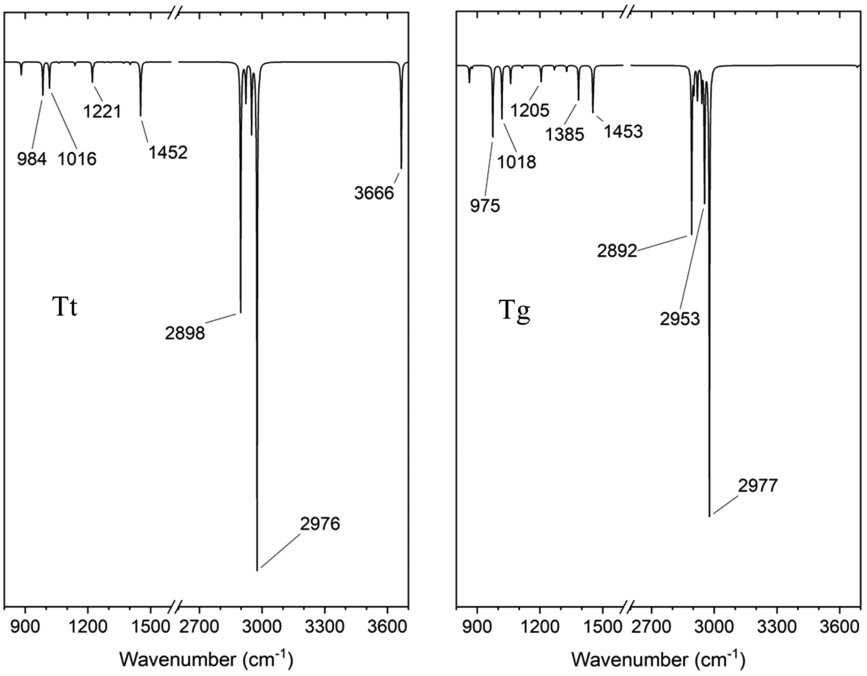

Figure 4. (Left) Simulated vibrational spectrum of the Tt conformer adsorbed on the Ag_{19} cluster. (Right) Simulated vibrational spectrum of the Tg conformer adsorbed on Ag_{19} cluster.

The simulated spectrum in Figure 3 gives a good match to the experimental spectrum. However, to obtain this match, the optimized geometry of the Tt conformer had to be altered slightly to reduce the intensity of the O−H stretch. This required rotation of the O−H bond by 17.2° to make it almost parallel to the surface. This decreased the calculated adsorption energy of the rotated Tt conformer (Tt_{rot}) by 0.64 kcal/mol. This decrease in calculated adsorption energy was due almost entirely to the way the molecule interacts with the Ag cluster, as rotation of the OH bond by the same amount for the gas phase Tt conformer raised the energy by only 0.17 kcal/mol. As shown in Tables S4−S6, the OH stretch intensity is almost the same for all gas phase conformers but varies considerably for the surface-bound conformers. This reflects not only the angle between the OH bond and the surface but also whether the OH bond is pointed toward the surface (negative angles), which leads to greater intensity, or away from the surface (positive angles), with different intensities for comparable magnitudes of the angles. Evidently, when the OH bond points toward the surface this increases the dipole derivative. This is most evident for the surface-bound Gg conformer, which has both the lowest OH stretch frequency and a calculated intensity a factor of 7 greater than that for the gas phase molecule.

Figure 4 compares the simulated spectra for the Tt and Tg conformers adsorbed on the Ag_{19} cluster at their optimized geometries. Although the general appearance of the two spectra is similar, with the two most intense peaks occurring in the C−H stretch region, there are also notable differences. For the Tg conformer, the O−H stretch is just barely visible, whereas it is the third most intense peak in the Tt spectrum. The frequencies are also shifted such that if both conformers were present in significant amounts, a spectrum with more peaks would be expected. The absence of an O−H stretch peak in the experimental spectrum would favor assigning it to the Tg conformer. However, the absence of any peak near 1385 cm^{-1}, due to a CH_2 twist mode, in the experimental spectrum of the monolayer argues against the Tg conformer. In the Supporting Information we show simulated spectra for the other three conformers. They all display prominent O−H stretch peaks as well as other deviations from the experimental spectrum of the monolayer and are thus ruled out. For example, in the Gg/Ag_{19} spectrum in Figure S1, the OH stretch is by far the most intense peak, which is completely incompatible with the experimental spectrum. In the spectrum of the Gt conformer on the Ag_{19} cluster (Figure S3), the most intense peak outside of the C−H stretch region is at 1199 cm^{-1}, due to the COH bending mode. Similarly, the spectrum of the Gg′ conformer on the Ag_{19} cluster (Figure S2) shows prominent peaks at 1195 and 1366 cm^{-1}, due to COH bend and CH_3 deformation modes. No peaks in this region are seen in the experimental spectrum.

There are several factors that can account for the discrepancies between the measured RAIR spectrum and the spectrum simulated for the conformer that was calculated to be most stably adsorbed. The differences in the adsorption energies between the different conformers surely exceed the accuracy of our DFT calculations. The most accurate theoretical calculations[11,13] of the relative energies of the gas phase 1-propanol conformers did not use DFT, but much more computationally intensive methods, that would not be feasible for even a small Ag_{19} cluster model of the Ag(111) surface. In contrast, the simulated spectra are distinctly different for each conformer, while the experimental spectrum was measured to very high precision. For this reason, obtaining a good match between the experimental and simulated spectra is a better way of identifying the conformational structure of the adsorbed molecule than relying on the calculated adsorption energies. Nevertheless, an exact match cannot be expected for several reasons. First, the experimental spectrum was obtained at a high coverage where adsorbate−adsorbate interactions would be expected to influence the orientation of

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the molecule. Second, anharmonicity is neglected in the simulated spectra and this can affect the positions of the peaks, as well as their relative intensities. Although a single scaling factor is used to bring the calculated harmonic frequencies into approximate agreement with experimental frequencies, which partly compensates for anharmonic shifts, it does so in an average way whereas each mode will have a different anharmonic constant and each pair of modes will be coupled by a different set of anharmonic terms. Third, using a finite cluster to model the surface could lead to inaccuracies in molecular orientation due to the influence of under-coordinated edge atoms. Despite these shortcomings in the theoretical simulation of the spectra, it was possible to associate the experimental spectrum with a single conformation for the adsorbed molecule.

It remains to consider the physical factors that determine the relative stability of the different conformers and how the interaction with the surface affects these factors. Kahn and Bruice explored the relative stability of the 1-propanol conformers at various levels of theory.[15] The predicted stability order at the Hartree−Fock limit is quite different from what is obtained when the effects of electron correlation are included. As a DFT calculation such as ours treats electron correlation quite differently than the more accurate methods, it is not surprising that the relative stabilities of the gas phase conformers that we calculate are different. Houk et al. explained the higher stability of the Gt conformer over the Tt conformer in terms of the electrostatic and polarization interactions between the methyl group and oxygen atom.[24] The electronegative O atom causes the methyl group of Gt to become more positive than Tt, which results in a stabilizing dipole−induced dipole interaction that is absent in the Tt conformer. However, the interaction with the surface evidently overwhelms these subtle effects that pertain to the gas-phase conformers. This is reflected by the larger energy differences for the adsorbed conformers than for the gas-phase ones. Although each conformer is coordinated to the surface via the O atom, this interaction is weak and van der Waals interactions between the propyl group and the surface will also contribute to the energy of adsorption and this interaction will be different for each conformer. However, the main reason a single conformer is preferred likely arises from the way the molecules pack together in the dense monolayer. The optimal packing arrangement would maximize adsorbate−adsorbate attractions and minimize repulsions. As our calculated optimal structures and adsorption energies do not include adsorbate−adsorbate interactions, we surmise that these interactions lead to an adsorption energy for the rotated Tt conformer that exceeds the adsorption energies for the other conformers by an amount that it is greater than the small energy differences among the isolated adsorbed conformers, which is already greater than the relative stability of the gas phase conformers.

CONCLUSIONS

The interaction of 1-propanol with the Ag(111) surface is characterized by an experimental IR spectrum with a few very sharp peaks despite the existence of multiple rotational conformers closely spaced in energy for the gas-phase molecule. Because each conformer has a distinctly different simulated IR spectrum, a mixture of different adsorbed conformers would be expected to yield a spectrum with many more peaks than observed. This indicates that interaction with the surface leads to the selective adsorption of a single conformer. The best match between the calculated and experimental spectra is for the Tt conformer, with the OH bond rotated from its optimized geometry to be nearly parallel to the surface plane.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.2c00817.

Simulated RAIR spectra for the Gg, Gg′, and Gt conformers of 1-propanol on a Ag_{19} cluster, simulated spectra for the gas-phase conformers, tables of additional calculated quantities, tables of calculated frequencies and assignments of all normal modes of the gas-phase and adsorbed conformers. (PDF)

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Notes

The authors declare no competing financial interest.

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