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Spectroelectrochemical and DFT Study of Squaric Acid Adsorption and Oxidation at Gold Thin Film and Single Crystal Electrodes

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Abstract

The adsorption and oxidation of squaric acid ($\text{H}_2\text{C}_4\text{O}_4$, H_2SQ) at gold single crystal and thin film electrodes with preferential (111) orientation were studied spectroelectrochemically in perchloric acid solutions. The existence of reversible adsorption-desorption processes in the double-layer region is reflected by structure-sensitive voltammetric features. IRRAS experiments carried out with Au(111) and Au(100) single crystal surfaces in 10 mM H_2SQ solutions show potential-dependent adsorbate bands at ca. 1780-1785 and 1511-1577 cm^{-1} for potentials below 1.00 V RHE. Increasing sensitivity of the ATR-SEIRA experiments allows the detection of similar features for much lower H_2SQ concentrations. According to DFT calculations, these bands can be assigned to adsorbed squarate anions which are bonded to the gold surfaces in a bidentate configuration through two oxygen atoms, with the molecular plane perpendicular to the metal surface. For 10 mM H_2SQ solutions, additional bands are detected in the ATR-SEIRA spectra at ca. 1630 cm^{-1} both in water and deuterium oxide solutions. Even if this frequency fits with one of the vibrational modes of adsorbed bisquarate, DFT calculations provide an alternative explanation for this potential-dependent feature that could be ascribed to collective vibrational modes of adsorbed squarate appearing at high adsorbate coverage. The existence of in-phase and out-of-phase contributions under these conditions would also explain the broadening and/or splitting of the observed bands. DFT calculations also show that squaric acid molecules adsorb very weakly at the gold surfaces and can be discarded as the origin of the observed infrared bands. The external reflection infrared spectra obtained for gold single crystal electrodes in the H_2SQ oxidation region show bands for dissolved carbon dioxide molecules as the main product. Bands for adsorbed bicarbonate anions formed from carbon dioxide are detected in the ATR-SEIRA spectra.

1. Introduction

Squaric acid (3,4-dihydroxycyclobut-3-ene-1,2-dione, $\text{H}_2\text{C}_4\text{O}_4$, H_2SQ) is a small cyclic organic compound belonging to the family of oxocarbons ($\text{H}_2\text{C}_n\text{O}_n$)^{1,2}. The existence of strong hydrogen bonds for the neutral oxocarbon molecules³, which determine their structures in solid crystals⁴ and in adsorbed phases⁵, and their high acid dissociation constant values^{1,6}, related to the electronic π -delocalization stabilizing the corresponding anions, are relevant characteristics of these compounds. Recent papers in the literature have described several applications and properties of squaric acid and its derivatives, including their role in a variety of biosensors^{7,8}, their use as synthons in bioorganic and medicinal chemistry⁹ and the formation of squaraine dyes¹⁰⁻¹³. Squaric acid (or squarate anions) have also been employed for the synthesis of metal nanoparticles^{14,15}, porous carbon microparticles¹⁶, 3D cube-shaped composites¹⁶ and porous alumina¹⁷.

Some experimental vibrational studies have been reported for squaric acid in the solid phase¹⁸⁻²⁰, where the formation of hydrogen bonds between neighbouring squaric acid molecules gives rise to layers containing the molecular cyclic structure⁴. An experimental and theoretical study of matrix-isolated squaric acid has also been reported²¹. The vibrational properties of squaric acid and its anions have been studied theoretically, both as isolated species^{22,23} and in solution^{23,24}, as well as experimentally²⁵.

The electrochemical reactivity of oxocarbons²⁶⁻³⁸, including that of squaric acid^{26-29,34,35,37,38} and some of its derivatives³⁹, has been described in water^{26,27,29-35,37,38} and in non-aqueous solvents^{28,36,39}. In aqueous solutions, most of the studies on the electrochemical oxidation of H_2SQ ^{26,27,29,34,35,38} and other oxocarbons^{26,30-33}, are related to their behaviour at platinum electrodes. It has been proved that oxocarbon electrooxidation at this electrode material is characterized by parallel reaction paths involving, in addition to their direct oxidation, their dissociative adsorption to form adsorbed carbon monoxide^{27,29-35,38}. This process leads to an effective blocking of the electrode surface for the hydrogen adsorption-desorption processes and is witnessed by the detection of C-O stretching bands in the in situ infrared spectra collected in the oxocarbon-containing solutions^{29,31-35,38}. In the case of squaric acid, the formation of adsorbates different from CO has been detected spectroscopically in a narrow potential window just above the onset of the oxidative stripping of the CO adlayer^{34,38}. The formed adspecies was tentatively identified as adsorbed squarate anions³⁴, this assignment being later confirmed by preliminary DFT (Density Functional Theory) calculations³⁸.

As a difference with the behavior described above for platinum, the electrochemistry of oxocarbons at gold electrodes is not expected to be determined by the formation of adsorbed CO

due to the weak adsorption of the latter species at this electrode material^{40,41}. In this way, Sant'Ana et al³⁷ reported in situ SERS (Surface Enhanced Raman Scattering) spectra for squaric acid adsorption at polycrystalline gold electrodes that showed only residual carbon monoxide bands. A variety of additional adsorbate features in the SERS spectra were assigned by the authors to adsorbed squaric acid and bisquarate species³⁷.

In a recent paper³⁸ we have presented new results regarding the electrochemical behavior of squaric acid at gold and platinum thin film electrodes. ATR-SEIRA (Surface Enhanced Infrared Reflection Absorption Spectroscopy under Attenuated Total Reflection conditions) spectra collected for the gold electrode showed potential-dependent bands in the double layer potential region related to the presence of adsorbates coming from squaric acid. The analysis of this kind of vibrational spectra on the basis of the experimental or calculated frequencies reported for squaric acid and its anions either in solid phase or as free species (gas or solution phases (see above)), is very limited, since bonding and structure significantly differ from the adlayers at the interfaces, as it is well established from some decades ago⁴². DFT calculations are needed as to determine the optimized geometries of these adsorbates, as a previous step for the calculation of their vibrational frequencies. In this way, a preliminary DFT study of adsorbed squarate at Au(111) surfaces provided optimized geometries with the molecular plane perpendicular to the metal surface and bonding to the gold surface through two oxygen atoms in a bidentate configuration³⁸. The corresponding calculated harmonic frequencies fit well with the observed experimental bands, thus supporting their assignment to adsorbed squarate anions. The goal of the present work is to expand the previous preliminary study to several aspects of the adsorption and oxidation behavior of H₂SQ at gold electrodes that still remain veiled. First, we focus on the structural effects on the adsorption behavior of H₂SQ by carrying out in situ IRRAS (Infrared Reflection Absorption Spectroscopy) experiments with Au(111) and Au(100) single crystal electrodes as well as DFT calculations for adsorbates coming from squaric acid (now including squaric acid (H₂SQ) and bisquarate anions (HSQ) together with squarate anions (SQ)) at gold surfaces with these orientations. Then, the effect of H₂SQ concentration on the nature of the adsorbed species will be explored. For this purpose, we will analyze the ATR-SEIRA spectra obtained with gold thin film electrodes with preferential (111) orientations because of the higher sensibility and lower interferences from dissolved species (including the solvent) in these internal reflection experiments when compared to IRRAS^{43,44}. The effect of deuteration on the infrared spectra of adsorbates coming for H₂SQ is also studied by comparing the results of spectroelectrochemical experiments in deuterium oxide solutions with the calculated harmonic spectra. The effect of adsorbate coverage on collective vibrational modes will be also explored in the case of adsorbed squarate.

2. Experimental

Au(111) and Au(100) single crystals were prepared by using Clavilier's method^{45,46} from quasi-spherical gold beads grown by melting a 99.9995 % gold (Alfa-Aesar) wire. The oriented surface of the samples used in voltammetric experiments were ca. 2 mm dia. whereas the diameters of the electrodes used in external reflection infrared experiments (IRRAS) were around 4.5 mm. Prior to each experiment, gold single crystal electrodes were flame-annealed, cooled down in air and protected with a droplet of ultrapure water⁴⁶⁻⁴⁸. A 25 nm-thick gold thin film (99.999%, Kurt J. Lesker Ltd.) thermally evaporated on one of the faces of a low oxygen-content silicon prism beveled at 60° (Pastec Ltd, Japan) was used as working electrode in the internal reflection infrared spectroscopy experiments (ATR-SEIRAS). Deposition was carried out in the vacuum chamber of a PVD75 (Kurt J. Lesker Ltd.) coating system at a base pressure around 10^{-6} Torr using a quartz crystal microbalance to control both the thickness of the gold film and the deposition rate (fixed at 0.006 nm s^{-1}). Once in the spectroelectrochemical cell, the gold thin film electrodes were cleaned by applying a few voltammetric cycles up to the onset of surface oxidation in the 0.1 M HClO_4 solution. Then, sodium acetate was added up to a 10 mM concentration to the working solution and an electrochemical annealing of the electrode surface was carried out by cycling the electrode potential at $20 \text{ mV} \cdot \text{s}^{-1}$ between 0.05 and 1.20 V for one hour⁴⁹. Subsequently, the spectroelectrochemical cell was thoroughly flushed with a 0.1 M HClO_4 until acetate anions were removed. Based on the preferential (111) orientation of the samples obtained with this procedure⁴⁹, the previously used Au(111)-25nm notation⁴³ will be employed also in this work.

All the voltammetric and in situ infrared experiments were performed in glass cells using a reversible hydrogen electrode (RHE) as the reference electrode and a gold wire as the counter electrode. Working solutions were prepared from solid H_2SO_4 (99% Acros Organics), concentrated perchloric acid (Merck Suprapur®) and ultrapure water ($18.2 \text{ M}\Omega \cdot \text{cm}$, TOC 50 ppb max, Elga Vivendi). In some experiments, solutions were prepared in deuterium oxide (99% D, Aldrich), which was used as received. Solutions were deaerated with Ar (N50, Air Liquide) and blanketed with this gas during the experiments. Voltammetric experiments were carried out with a CHI660D workstation.

In situ infrared experiments were carried out with a Nexus 8700 (Thermo Scientific) spectrometer equipped with a MCT-A detector and a wire grid ZnSe polarizer (Pike Tech). The spectroelectrochemical cell^{50,51}, equipped with a CaF_2 (IRRAS) or with a Si (ATR-SEIRAS) window beveled at 60°, was placed at the top of a Veemax (Pike Tech.) reflectance accessory. All the potential-dependent spectra were collected with a resolution of 8 cm^{-1} and are presented

in absorbance units (a.u.) as $-\log(R/R_0)$, where R and R_0 represent, respectively, the reflectivities at the sample and reference potentials. Thus, positive and negative bands correspond, respectively, to gain or loss of species at the sample potential with respect to the reference potential. In most of the experiments, the electrode was stepped from the reference to the sample potential and 100 interferograms were collected at each potential. Dynamic experiments were also carried out in which the spectra were collected in a rapid scan mode while the electrode potential was swept at $2 \text{ mV}\cdot\text{s}^{-1}$. In these experiments, each spectrum was the average of a set of 104 interferograms which were collected in ten seconds, thus corresponding to a 20 mV interval. All the spectra are referred to the reference single beam spectrum collected in the H_2SQ -containing solutions at 0.10 V.

3. Computational details

Geometry optimization and harmonic frequency calculations were carried out for H_2SQ , HSQ and SQ species adsorbed on periodic models for the $\text{Au}(111)$ and $\text{Au}(100)$ surfaces. All calculations were done within the DFT-GGA approach of Perdew, Burke and Ernzerhof^{52,53}, as implemented in the VASP code⁵⁴⁻⁵⁷, using the Projector-Augmented-Wave method^{58,59}, and a cutoff energy value of 400 eV.

The simulation cells contained a slab formed by 4 metallic layers (with either 9 or 16 Au atoms each), with (3x3) and (4x4) surface periodicities, for a total of 36 and 64 metal atoms respectively. A vacuum region of more than 1.2 nm was included, in order to avoid any significant coupling between the adsorbate species and the back side of the slab. The positions of the Au atoms were kept fixed, with a nearest-neighbour distance of 0.29521 nm (lattice constant equal to 0.41748 nm). These values, that were obtained from the fit of the calculated bulk energy vs. bulk volume curve to a Murnaghan equation of state, agree well with those reported in other PBE calculations, and with the experimental value (0.4065 nm for the lattice constant of pure gold)⁶⁰.

Sampling of the k-points in the first Brillouin zone used an automatic Monkhorst-Pack⁶¹ (3x3x1) scheme. Second order Methfessel-Paxton⁶² smearing was used with $\sigma=0.2 \text{ eV}$. As convergence criteria we used: 10^{-5} eV for the electronic energy, and forces on atoms below 0.02 eV/Angstrom, for the geometry optimization (with no symmetry restriction) of the molecular adspecies. The calculated vibrational frequencies were obtained using the harmonic approximation, with atomic displacements of 0.015 Angstrom for each coordinate. All calculated frequency values are reported without scaling. Their relative errors are estimated from previous work^{63,64} to be below 2-3% of the calculated frequency value. For most calculations, and unless otherwise stated, the (3x3) simulation cell contained only one adsorbate

species on one side of the slab, this situation corresponding to the low coverage limit ($\theta = 1/9$), where lateral interactions between adsorbates are expected to be minimal or almost negligible. Additional calculations were carried out for SQ adlayers with surface coverage equivalent to $1/16$, $2/9$ and $1/3$ adsorbate species per surface metal atom (see below for details).

Optimized geometries and vibrational modes were visualized using Molden⁶⁵ and Jmol⁶⁶.

Figure 1. Optimized adsorption geometries of A) Squaric acid (H_2SQ), B) Bisquarate (HSQ) and C-E) Squarate (SQ) species adsorbed at $\text{Au}(111)$ with A-C) $\theta=1/9$, D) $\theta=2/9$ and E) $\theta=1/3$

4. Results and discussion.

4.1. DFT calculations for adsorbed H₂SQ, HSQ and SQ.

4.1.1. Optimized adsorbate geometry.

Geometry optimization calculations were carried out for undissociated squaric acid (H₂SQ), hydrogensquarate (bisquarate, HSQ) and squarate (SQ) species on Au(100) and Au(111) model surfaces. The optimized adsorbate bonding configurations are shown in Figures 1 A-C. For the three species, the bonding to the surface has a bidentate configuration involving two oxygen atoms that are linked to two nearest neighbor surface gold atoms. For the three species the plane of the carbon ring is perpendicular to the metal surface and aligned with the surface dense metal rows. Some configurations were also observed that showed a slight twist of the molecular plane with respect to the dense rows. The energies of the latter configurations were not significantly different from the well aligned one. As these configurations also give rise to the same calculated vibrational features, we will not refer to them in the following. Note that the orientation of the molecular plane in the optimized geometries allows for the observation of adsorbate-specific vibrational modes, provided that the surface selection rule is fulfilled for the particular vibration movement. DFT calculations were also carried out starting from unidentate configurations on top, bridge and hollow positions of the Au(111) model surfaces. All these calculations ended with the organic species far from the surface, indicating that unidentate adsorption is not favoured for these adsorbates.

Table 1 summarizes selected structural parameters for the optimized adsorbate geometries. A first, important difference between the optimized geometries of H₂SQ and the other two adsorbate species is the distance between the Au surface atoms and the nearest oxygen atoms in the organic. The value of 305 pm obtained for H₂SQ is greater than those for HSQ and SQ, that are close to 240 pm. The former value is significantly higher than those reported for other O-link chemisorption cases^{67,68}. This indicates that the interaction between H₂SQ and the metal is weak, and physical in nature, as the formation of a chemical bond to the metal involving the lone pair electrons of the carbonyl oxygen is not favorable. On the other hand, for both HSQ and SQ the Au-O distances agree with a chemisorption situation. On this basis, H₂SQ is not expected to compete effectively with HSQ, SQ and even the water molecules, for the adsorption sites on the metal surface.

Table 1. Optimized bond lengths and angles for squaric acid (H_2SQ), bisquarate (HSQ) and squarate (SQ) adsorbed on Au(111).

	H_2SQ	HSQ	SQ
d Au-O / pm	309 / 303	236 / 244	244 / 239
$\angle$ Au-Au-O / $^\circ$	93.5 / 92.5	91.6 / 92.6	91.8 / 95.4
d O_{ad} -C / pm	121 / 121	126 / 124	124 / 124
$\angle$ Au-O-C / $^\circ$	128.4 / 127.9	129.0 / 129.9	131.1 / 129.7
$\angle$ O-C-C / $^\circ$	137.9 / 138	136.0 / 131.1	139.9 / 136.0
d C-C / pm	156	150	147
d C-C' / pm	149 / 149	143 / 153	151 / 151
d C'-C' / pm	139	146	156
d C-O(H) / pm	133 / 133	132	-
$\angle$ C-O-H / $^\circ$	112.8 / 112.7	120.0	-
d C=O / pm	-	122	121 / 121

For simplicity, values for some parameters involving carbon atoms either far or close to the metal have been grouped in pairs. C' denotes the two carbon atoms that are farthest from the metal surface, as to distinguish from the carbon atoms bonded to the oxygen linked to the metal.

Some other significant differences can be observed in the set of structural parameters reported in Table 1. The O_{ad} -C distance, that for the physisorbed H_2SQ amounts to 121 pm (which is typical of a carbonyl bond) increases to 124-126 pm for the other two species considered. This indicates a weakening of the C- O_{ad} bond, that correlates well with the decrease in bond length for the C-C link that is parallel and closer to the metal surface: 156 pm for H_2SQ , 150 pm for HSQ, and 147 pm for SQA. This trend is in agreement with a transition from a single C-C bond in H_2SQ towards a double-bond-like character in SQ. We have to recall here that the shortening in the C-C bonds in the free SQ anion is related to the aromatic character of this species. Incidentally, it must be noted also that SQ anion and cyclobutanetetrone (C_4O_4) can be considered as identical from their elemental composition, differing only in their net electrical charge. The intrinsic 4-fold symmetry of the structure of the isolated SQ species is broken upon bonding to the gold surface. This is evidenced by the different C-C bond lengths observed for adsorbed SQ: 147 pm for the CC bond parallel and closer to the metal surface, 156 pm for the other CC bond parallel to the surface and 151 pm for both CC bonds perpendicular to the surface. The C-O bond length is 121 pm for the part of the molecule not directly coordinated to the metal, and 124 pm for that involved in the link to the Au surface atoms through the oxygens. This geometry resembles that expected for species with two true carbonyl moieties facing

toward the vacuum part of the simulation cell, and an enolic vic-diol-like part involved in the bidentate chemisorption configuration.

For H₂SQ and SQ some differences are observed for the values of bond lengths and angles that would be expected to be identical. See, for instance, the pair of values of the Au-O-C angles for H₂SQ and SQ in Table 1. These small variations arise from the lack of imposed symmetry constraints in the geometry optimization procedure. On the other hand the presence of different oxygenated groups (carbonyl and enolic hydroxyl) on the HSQ adsorbate are at the origin of much more important differences in the C-C' bond distances (143 and 153 pm), that reflect the difference in bond order and the intrinsic asymmetry of the adsorbate structure.

4.1.2. Harmonical vibrational frequencies.

The calculated harmonic frequencies obtained for the optimized adsorbate geometries of H₂SQ, HSQ and SQ in the experimentally available spectral range (between 4000 and 1000 cm⁻¹) and the mode assignment (main contributions) are summarized in Tables 2 to 5. Results for H₂SQ and HSQ (Tables 2 and 3, respectively) include those for the corresponding deuterated species and were obtained for a surface coverage of 1/9 for both Au(111) and Au(100) surfaces. Results for adsorbed SQ at Au(111) and Au(100) surfaces are reported, respectively, in Tables 4 and 5 also for coverage values of 1/16, 2/9 and 1/3 adspecies per surface metal atom. The reported results complement previously published data for SQ at Au(111) and Pt(111) surfaces for $\Theta=1/9$ ³⁸.

Comparison of the calculated frequencies for each of the three adsorbate species on the Au(111) and Au(100) surfaces shows that their values are very similar. In the case of H₂SQ, the differences are marginal, even smaller than the experimental uncertainty. In the case of HSQ, the calculated frequencies are also fairly similar on both surfaces, with the maximum difference corresponding to the band corresponding to the asymmetric O_{ad}CCO_{ad} stretch (the subscript ads refers to the metal-coordinated O atoms) in combination with the C=O stretch (1575 cm⁻¹ for Au(111), 1560 cm⁻¹ for Au(100)). For the SQ adspecies, the maximum shift due to crystallographic orientation amounts to 12 cm⁻¹, also for the asym O_{ad}CCO_{ad} mode. On the basis of the high similarity of the calculated band frequencies irrespective of the crystallographic orientation of the metal surface, we will focus in the following on the discussion and interpretation for the case of Au(111), as the ATR-SEIRAS experiments with gold thin film electrodes having this preferential orientation provide more detailed information with a much better signal-to-noise ratio, and are free from contributions coming from species in solution, in particular from the solvent ^{43,44}.

Table 2. Calculated harmonic vibrational frequencies and band assignment for H₂SQ and D₂SQ adsorbed on Au(111) and Au(100) model surfaces. Adsorbate surface density corresponds to 1 species per 9 surface metal atoms.

	H ₂ SQ		D ₂ SQ	
Assignment	Au(111)	Au(100)	Au(111)	Au(100)
ν OH, out-of-phase	3654	3654	2658	2659
ν OH, in-phase	3634	3641	2646	2650
Sym ν OCCO	1820	1819	1819	1818
Asym ν OCCO	1763	1758	1763	1757
ν C=C	1603	1610	1612	1609
ν C-O + δ COH	1416	1417	1378	1382
δ COH (in-phase) + ν CC	1302	1299	1156	1157
δ COH (out-of-phase) + ν CC	1208	1208	1108	1109

Table 3. Calculated harmonic frequencies and band assignments for HSQ and DSQ adsorbed on Au(111) and Au(100) surfaces. Adsorbate surface density corresponds to 1 species per 9 surface metal atoms.

	HSQ		DSQ	
Assignment	Au(111)	Au(100)	Au(111)	Au(100)
ν OH	3612	3613	2628	2628
ν C=O + sym ν O _{ad} CCO _{ad}	1781	1786	1779	1785
Sym ν O _{ad} CCO _{ad} + ν C=O	1657	1650	1654	1649
Asym ν O _{ad} CCO _{ad} + ν C=O	1575	1560	1572	1560
ν C-O + sym ν O _{ad} CCO _{ad}	1439	1442	1430	1427
δ COH + ν CC	1309	1307	1209	1202
CC + δ COH	1068	1058	1004	959

As the main point of discussion of the experimental infrared spectra regards the nature of adsorbates giving rise to the observed bands, we must focus on the existence of specific

vibrational modes for the various chemisorbed species that could be formed from squaric acid (namely H_2SQ , HSQ or SQ) at the gold electrode surfaces. The possibility of detecting adsorbed H_2SQ spectroscopically will be discussed despite of its weak adsorption at gold electrodes (see above). It has to be recalled here that, in order to be infrared active, the vibrational modes for adsorbates at metals must have a transition dipole moment with a non-zero component normal to the metal surface in order to fulfill the surface selection rule for external reflection⁶⁹ and SEIRAS⁷⁰ experiments. The comparison of the calculated harmonic frequencies for a surface concentration equivalent to one adsorbate per 9 surface gold atoms shows that absorption from HSQ and SQ species is expected around $1760\text{-}1780\text{ cm}^{-1}$. In the case of SQ , it would be related to the symmetric OCCO stretch of the uncoordinated moiety, as the corresponding asymmetric mode has a transition dipole essentially parallel to the metal surface. The same holds for the asymmetric OCCO mode of adsorbed H_2SQ . For this latter species, the corresponding symmetrical mode would appear at ca. 1820 cm^{-1} . The HSQ adsorbate presents a calculated frequency around $1650\text{-}1660\text{ cm}^{-1}$ corresponding to a combined mode involving the stretch of the carbonyl group and the symmetric stretch of the $\text{O}_{\text{ad}}\text{CCO}_{\text{ad}}$ moiety bonded to the metal. This vibrational mode would be observable experimentally on the basis of the surface selection rule.

Both HSQ and SQ , but not H_2SQ , have theoretical frequencies around $1560\text{-}1580\text{ cm}^{-1}$ corresponding to experimentally observable vibration modes. Again, the calculated frequency around $1520\text{-}1530\text{ cm}^{-1}$ for the asymmetric $\text{O}_{\text{ad}}\text{CCO}_{\text{ad}}$ mode of adsorbed SQ would not be observable, as has its transition dipole essentially parallel to the metal surface. In the spectral region between 1200 and 1500 cm^{-1} no vibrational feature is expected for the SQ adsorbate. However, two modes of adsorbed HSQ have frequencies around 1440 and 1310 cm^{-1} . On the basis of the calculated frequencies for the deuterated case, these two latter modes are the only ones undergoing a frequency redshift upon deuteration. Finally, both adsorbed HSQ and SQ species have calculated frequencies around $1060\text{-}1080\text{ cm}^{-1}$, in a region where adsorbed perchlorate anion also absorbs.

Table 4. Calculated harmonic frequencies and band assignments for SQ adsorbed on $\text{Au}(111)$ at various coverages.

Au(111)							
$\Theta = 1/16$		$\Theta = 1/9$		$\Theta = 2/9$		$\Theta = 1/3$	
ν / cm^{-1}	Assign	ν / cm^{-1}	Assign	ν / cm^{-1}	Assignment	ν / cm^{-1}	Assignment
1768	Asym ν OCCO	1777	Asym ν OCCO	1791 1788	Asym ν OCCO out of phase Asym ν OCCO in-phase	1825 1810, 1810	Asym ν OCCO in-phase Asym ν OCCO out of phase
1751	Sym ν OCCO	1768	Sym ν OCCO	1787 1734	Sym ν OCCO in-phase Sym ν OCCO out of phase	1790 1714, 1712	Sym ν OCCO in-phase Sym ν OCCO out of phase
1556	Sym ν $\text{O}_{\text{ad}}\text{CCO}_{\text{ad}}$	1566	Sym ν $\text{O}_{\text{ad}}\text{CCO}_{\text{ad}}$	1587 1569	Sym ν $\text{O}_{\text{ad}}\text{CCO}_{\text{ad}}$ in-phase Sym ν $\text{O}_{\text{ad}}\text{CCO}_{\text{ad}}$ out of phase	1632 1627	Asym ν $\text{O}_{\text{ad}}\text{CCO}_{\text{ad}}$ in-phase Sym ν $\text{O}_{\text{ad}}\text{CCO}_{\text{ad}}$ in-phase
1527	Asym ν $\text{O}_{\text{ad}}\text{CCO}_{\text{ad}}$	1530	Asym ν $\text{O}_{\text{ad}}\text{CCO}_{\text{ad}}$	1540 1538	Asym ν $\text{O}_{\text{ad}}\text{CCO}_{\text{ad}}$ in-phase Asym ν $\text{O}_{\text{ad}}\text{CCO}_{\text{ad}}$ out of phase	1610, 1608 1588, 1587	Asym ν $\text{O}_{\text{ad}}\text{CCO}_{\text{ad}}$ out of phase Sym ν $\text{O}_{\text{ad}}\text{CCO}_{\text{ad}}$ out of phase
1076	ν CC	1080	ν CC	1083 1082	ν CC in-phase ν CC out of phase	992 990, 989	ν CC in-phase ν CC out of phase

Table 5. Calculated harmonic frequencies and band assignments for SQ adsorbed on Au(100) at various coverages.

Au(100)			
$\Theta=1/9$		$\Theta=1/3$	
ν / cm^{-1}	Assign.	ν / cm^{-1}	Assignment
1772	Asym ν OCCO	1820	Asym ν OCCO in-phase
		1804, 1804	Asym ν OCCO out of phase
1762	Sym ν OCCO	1781	Sym ν OCCO in-phase
		1719, 1718	Sym ν OCCO out of phase
1558	Sym ν O _{ad} CCO _{ad}	1618	Asym ν O _{ad} CCO _{ad} in-phase
		1609	Sym ν O _{ad} CCO _{ad} in-phase
1518	Asym ν O _{ad} CCO _{ad}	1595, 1595	Asym ν O _{ad} CCO _{ad} out of phase
		1577, 1575	Sym ν O _{ad} CCO _{ad} out of phase
1083	ν CC	986, 986	ν CC out of phase
		985	ν CC in-phase

The effect on the calculated band frequency values of adsorbate coverage, which experimentally depends both on solution concentration and electrode potential, was studied for the squarate anion on both the Au(111) and Au(100) surfaces. Optimized adsorption geometries and harmonic vibrational frequencies were obtained for surface coverage of 1/16, 1/9, 2/9 and 1/3 (expressed as the ratio of adsorbate species per surface metal atom) at Au(111) surfaces and 1/9 and 1/3 in the case of Au(100). In particular, for the 2/9 and 1/3 coverage we restricted ourselves to configurations in which all the molecules were parallel, without any relative shift in the direction of molecular ring plane. These configurations are shown in Figures 1D-E for Au(111), and the frequencies and band assignments in Tables 4 and 5 for Au(111) and Au(100), respectively. Because of the periodic boundary conditions needed for the calculations, the case of coverage 1/3 corresponds to a periodic array of infinite rows of parallel stacking SQ species adsorbed perpendicular to the electrode surface, each bonded to two nearest neighbor Au atoms through two oxygen atoms. Separating two neighbouring SQ stack arrays, there is a row of surface Au atoms free of adsorbates. These adlayer model arrangements have been chosen as to probe, in a computationally economical way, the effect of the collective dipole couplings on the vibrational frequencies of the adsorbates and are far from fully depicting the actual complexity of real SQ adlayers (that could also incorporate some adsorbed HSQ). Other phenomena can be envisaged as giving rise to modifications in the vibrational behavior of these systems. For instance, the formation of hydrogen bonding between either adsorbates coming from squaric acid or with water molecules either in contact with the metal or in a second layer. These effects

are out of the scope of this study and have not been considered, because of the increased computational cost.

The increase in SQ coverage leads to coupling of the vibrational motions of nearest-neighbouring SQ species, originating collective vibrational modes, in which the movements corresponding to a given normal mode in different molecules can be either all-in-phase, or with different degrees of dephasing (depending on the size of the sample). As reflected by the data reported in Tables 4 and 5 for Au(111) and Au(100), respectively, this behavior would give rise to a splitting of the OCCO bands for adsorbed squarate with a concomitant and increasing blue shift of the band frequency for the in-phase mode when coverage increases from 1/9 to 2/9 or 1/3. This shift is smaller for the symmetric OCCO mode of the coordinated moiety (from 1768 to 1790 cm^{-1} in the case of Au(111)) when compared to that of the coordinated one (from 1566 to 1627 cm^{-1} (also for Au(111))). Again, the shift associated to asymmetric modes would not be observed due to the surface selection rule. On the other hand, the decrease in coverage down to 1/16 yields harmonic calculated frequencies slightly lower than for the reference case of 1/9 SQ adsorbate per surface gold atom.

4.2. Experimental results

4.2.1. Au(111) and Au(100) electrodes

Figures 2A and B show cyclic voltammograms obtained, respectively, with Au(111) and Au(100) electrodes in 0.1 M HClO_4 solutions containing H_2SQ concentrations ranging from 0 to 10 mM. The stationary voltammograms recorded up to 0.90 V for each H_2SQ concentration (which, for the flame annealed electrodes, are obtained in the second and subsequent voltammetric cycles) are reported in the corresponding insets. The increasing voltammetric charges observed in this potential region when increasing the H_2SQ concentration indicate the existence of reversible adsorption-desorption processes linked to the presence of H_2SQ and/or its anions. It must be recalled that, taking into account the solution pH (around 1.0) and the pKa values for H_2SQ (0.54 and 3.48⁸), squaric acid and bisquarate anions are the prevailing species in solution. The detected adsorption/desorption processes, which appear at less positive potentials in the case of the Au(100) electrode surface when compared with Au(111), are shifted to lower electrode potentials for higher H_2SQ concentrations. It can be remarked that the shape of the cyclic voltammograms previously reported for a polyoriented gold electrode, which are characterized by two wide voltammetric features centered at ca. 0.25 and 0.60 V³⁸, seems to be linked to the contributions of (100) and (111) surface sites. Besides, a pair of small sharp

voltammetric features observed at ca. 0.83 V in the 10 mM H₂SQ solution for the polyoriented gold surface, which are well-developed for the Au(111) electrode surface (see the inset in Figure 2A), can be related to the presence of atomically flat (111) facets³⁸. This voltammetric feature, that is not observed for the Au(100) electrode, is similar to that reported in sulphuric⁴³ and cyanuric acid⁶³ solutions for gold electrodes with (111) wide domains and can be tentatively ascribed, as for the former systems, to an order-disorder transition within the adsorbate adlayer⁴³.

Once the voltammetric curves reported in the insets of Figure 2A and B were recorded, the upper limit of the potential scan was increased up to 1.7 V. Voltammetric profiles show the occurrence for potentials above 1.0 V of irreversible oxidation processes involving squaric acid and/or its anions (see also Figures 2A and B). In the case of the Au(111) electrode in contact with 0.01 and 0.1 mM H₂SQ solution, an oxidation peak appears at ca. 1.11 V, followed by a current tail at higher potentials (curves b and c in Figure 2A). Note that the peaks at ca. 1.34 and 1.55 V in the voltammograms reported in Figure 2A are those characteristic of the oxidation of the Au(111) electrode in perchloric acid solutions^{46,47} (see curve a). The H₂SQ oxidation peak at ca. 1.11 V in curves b and c grows and shifts up to ca. 1.18 V for the 10 Mm H₂SQ solution (curve e). Besides, another oxidation peak appears for the Au(111) electrode at ca. 1.26 V for the 1 mM solution (curve d). This voltammetric feature appears at 1.43 V as the main oxidation peak when H₂SQ concentration is increased up to 10 mM. For Au(100), an squaric acid oxidation peak appears at ca. 1.10 V for the lower H₂SQ concentrations (see curves b and c in Figure 2B). A broad oxidation peak centered at ca. 1.35 V is the main oxidation feature for the 10 Mm H₂SQ solution with a shoulder at ca. 1.17 V (curve e). All these features overlap with the currents due to the oxidation of the Au(100) surface appearing between 1.30 and 1.70 V^{46,47}.

Figure 2. Cyclic voltammograms obtained for Au(111) and Au(100) electrodes in a x mM H_2SQ + 0.1 M HClO_4 solutions. The insets show the second voltammetric cycles recorded for the flame-annealed electrodes in the double layer region before the subsequent cycles up to 1.70 V. x= a) 0; b) 0.01 ; c) 0.1 ; d) 1 ; e) 10 . Sweep rate: $50 \text{ mV} \cdot \text{s}^{-1}$.

The comparison of the voltammetric profiles reported in Figure 2 for the Au(111) and Au(100) electrodes in the 10 mM H_2SQ solution shows that the onset of H_2SQ oxidation takes place at potentials slightly lower for the Au(100) and with higher current maxima (when comparing the main oxidation peaks) than for the Au(111) electrode. For both orientations, an inhibiting effect of the gold surface oxide on the kinetics of the squaric acid oxidation reaction could contribute to the decreasing currents at potentials above 1.40 V.

Figure 3. Potential-difference IRRA spectra collected for Au(111) and Au(100) gold single crystal electrodes with p-polarised light in a 10 mM H_2SQ + 0.1 M HClO_4 solution prepared in water. Spectra for potentials up to 0.90 V were collected in potential step experiments whereas those for higher electrode potentials are extracted from a series of spectra collected during a potential scan from 0.10 to 1.70 V RHE (see text for details). In all cases, the reference spectrum was collected at 0.10 V in the same solution. 100 or 104 interferograms were coadded in the potential-step and potential-scan experiments, respectively, with a spectral resolution of 8 cm^{-1} .

External reflection infrared experiments were carried out with Au(111) and Au(100) electrodes in 10 mM H_2SQ solutions prepared in water. The spectra reported in Figures 3A and B were obtained with p-polarized light for various sample potentials. The spectra for potentials up to 0.90V were collected during potential step experiments and show positive-going bands, related to species being generated at the indicated sample potentials, at ca. 1780-1785 and 1511-1577 cm^{-1} . These bands appear for potentials above 0.40-0.50 V in the case of Au(100) and above 0.60-0.70 V for Au(111), being partially overlapped with a band at ca. 1640 cm^{-1} that could be related to the OH bending mode of uncompensated water molecules. Except for this latter feature, the observed potential-dependent band scan be associated to squaric acid or related species. The potential-dependent frequency shift of these bands (see below) is typical of coverage- and/or potential effects on the band frequency of adsorbed species. Moreover, and

taking into account the surface selection rule for external reflection infrared experiments⁶⁹, the absence of these bands in the spectra collected with S-polarized light (not shown) is also consistent with the assignment of the bands at 1780-1785 and 1511-1577 cm^{-1} to adsorbed species at the electrode surface. In connection to DFT results reported in section 4.1.2, it can be noted that adsorbate bands at ca. 1780-1785 and 1511-1577 cm^{-1} have frequency values which are similar for Au(100) and Au(111) electrodes and fit in a first approach to the calculated values for symmetric OCCO and $\text{O}_{\text{ad}}\text{CCO}_{\text{ad}}$ vibrational modes of adsorbed squarate or bisquarate species. Consistently with its weak adsorption, no band is observed at ca. 1820 cm^{-1} that could be related to the symmetric OCCO of adsorbed H_2SQ . An eventual contribution of the corresponding asymmetric mode to the band at ca. 1511-1577 cm^{-1} can be discarded due to the surface selection rule. Regarding the eventual existence of features that could be related to the presence of adsorbed HSQ at the gold electrodes, it has to be noted that the observation of bands around 1630 cm^{-1} is hindered by the overlapping of uncompensated OH bending bands for interfacial water. In the same respect, no clear bands can be observed in the spectral region between 1500-1300 cm^{-1} where adsorbed bisquarate presents some vibrational modes according to DFT calculations (see table 3). More insight on the assignment of the observed adsorbate bands would be given from the analysis of the results of the ATR-SEIRA experiments for gold thin film electrodes, which provide spectra with a better signal-to-noise ratio and almost free from water interferences.

In order to explore also the squaric acid oxidation region, additional experiments were carried out in which the potential applied to the Au(111) and Au(100) electrodes was scanned at 2 $\text{mV}\cdot\text{s}^{-1}$ from 0.10 V up to 1.70 V (see the experimental section for details). Selected spectra obtained at potentials above 0.90 V are reported in the upper part of Figures 3A and B. Note that the spectra obtained at potentials from 0.10 to 1.0 V in these experiments are basically equal to those obtained in potential step experiments. The slightly lower signal-to-noise ratio in the potential scan spectra is caused by the faster interferometer scan rate used in rapid scan experiments. Note also that the spectra for an electrode potential of 1.00 V are still similar to those recorded at 0.90 V for each electrode, suggesting the existence of similar adsorbate coverages in agreement with the lack of significant oxidation currents at potentials between 0.90 and 1.00 V in Figure 2. However, for potentials above 1.00 V, the intensity of adsorbate bands described above starts to decrease, disappearing completely for potentials above 1.10 V for Au(111) and 1.20 V for Au(100). The spectra at potentials higher than 1.00 V show an additional band at ca. 2343 cm^{-1} related to the asymmetric OCO stretching of the dissolved carbon dioxide molecules formed upon the irreversible oxidation of H_2SQ and related species. As a typical characteristic of the external reflection experiments, the produced CO_2 molecules are trapped in the thin solution layer between the electrode surface and the infrared window.

The spectra collected at potentials above 1.20 V show another small positive band at ca. 1415-1420 cm^{-1} that can be associated to adsorbed (bi)carbonate anions formed from dissolved carbon dioxide⁷¹. Decoupled mass transport from the outer solution is also responsible for the negative bands at ca. 1805, 1558 and 1481 cm^{-1} related to dissolved H_2SQ and HSQ molecules consumed upon oxidation^{29,34}. No other band associated to either adsorbed or dissolved species formed as an squaric acid oxidation product was detected.

Figure 4. Potential-dependent band frequencies (upper panels) and integrated band intensities (lower panels) for the features appearing in the external reflection infrared spectra collected for A) Au(111), B) Au(100) and C) Au(111)-25 electrodes during a potential scan experiment in x mM H_2SQ + 0.1 M HClO_4 solutions prepared in water. (★,▲,+) Bands for adsorbed squarate ; (✕,●) Bands for carbon dioxide and adsorbed bicarbonate (see text). A,B) x 0.10 ; C) x= 0.1 (open symbols) and 10 (solid symbols). The plots for the band at ca. 1630 cm^{-1} in panels C correspond to the spectra collected in a 10 mM H_2SQ solution in D_2O .

The potential-dependent behavior of the integrated band intensities and band frequencies of the spectral features described above can be analyzed with more detail with the help of the

corresponding plots reported in Figure 4A and B for Au(111) and Au(100) electrodes, respectively. In order to cover the whole potential range from 0.10 to 1.70 V, the plotted values are those obtained from the spectra measured during the potential scan experiments in the 10 mM H₂SQ solution. No significant differences were observed between the data obtained from the spectra collected in potential step or potential scan experiments in the potential range from 0.10 to 0.90 V. As mentioned above, and in agreement with the voltammetric profiles shown in Figure 2, the plots in Figure 4A and B show that the positive bands at ca. 1780-1785 and 1511-1577 cm⁻¹ appear at less positive potentials for Au(100) in comparison with Au(111). Figure 4B also shows higher integrated intensity values for Au(100). It can also be appreciated in Figure 4A and B that the frequencies of these bands shift to higher wavenumber when increasing the electrode potential, with a higher tuning rate in the case of the band at ca. 1511-1577 cm⁻¹. This behavior was discussed previously for gold and platinum thin film electrodes and related to an expected greater effect of the potential-dependent changes in the electronic surface state on the coordinated O_{ad}CCO_{ad} moiety (associated to the band at ca. 1511-1577 cm⁻¹) when compared to the non-coordinated one (band at ca. 1780-1785 cm⁻¹) ³⁸. As mentioned above, the integrated intensity of the adsorbate bands at the onset of squaric acid oxidation (i.e. around 1.10 V) are higher for Au(100) when compared with Au(111), for which adsorbate coverage falls to an almost zero value. Plots for the integrated intensity of the carbon dioxide band show higher values at 1.10 V for Au(111) when compared with Au(100), in agreement with the slight negative shift of the onset of H₂SQ oxidation for Au(100) in comparison to Au(111) that can be observed in Figure 2. The observation of significantly higher integrated band intensity values for Au(111) for all potentials above 1.00 V correlate also with the higher peak current density observed for this orientation. The potential-dependent behavior of the bicarbonate band at ca. 1420 cm⁻¹ reflects the formation of this adsorbate from trapped carbon dioxide molecules and its subsequent desorption at the higher electrode potentials, for which hydroxide and oxide adsorption prevails at the gold electrode surface⁷¹.

4.2.2. Gold thin film electrodes

Curves b and c in Figure 5 show cyclic voltamograms obtained for a Au(111)-25 nm thin film electrode in 0.1 and 10 mM H₂SQ solutions, respectively. These curves can be compared in the same figure with that recorded for the H₂SQ-free perchloric acid solution (curves a). Curves in the double layer region (see the inset) are similar to those shown in Figure 2 for Au(111) and Au(100) electrodes regarding the excess of voltammetric charge associated to the presence of squaric acid in the working solution. Note that, in agreement with its preferential (111) orientation, most of the voltammetric charge associated to the presence of squaric acid appears

at potentials above 0.40 V. Besides, a spike at ca. 0.86 V is observed in the 10 mM H₂SQ solution that can be related to the presence of ordered (111) domains at the surface of the Au(111)-25 nm film electrodes. The slightly more positive potential (0.86 vs 0.83 V) and lower peak current density values for this feature when compared to those observed for the Au(111) electrode can be related to the existence of narrower (111) domains for the gold thin film⁴³. Regarding the H₂SQ oxidation features, a peak appears at 1.13 V for the 1 mM H₂SQ solution together with a second small oxidation peak at ca. 1.58 V. For higher H₂SQ concentrations, the intensity of these peak sincreases as they shift to more positive potentials, appearing at ca. 1.25 and 1.66 V, respectively. Differences in the shape of the oxidation peaks in Figures 2A and 5 can be related to the existence at the Au(111)-25 nm electrode surface of a significant amount of sites in step domains and/or with symmetries other than (111).

Figure 5. Cyclic voltammograms obtained for a Au(111)-25nm thin film electrode in x mM H₂SQ + 0.1 M HClO₄ solutions. The inset shows the stationary voltammetric cycles recorded in the double layer region before the subsequent cycles up to 1.70 V. x= a) 0; b) 0.1; c) 10. Sweep rate: 50 mV·s⁻¹.

ATR-SEIRAS experiments have been carried out with Au(111)-25 nm electrodes in 0.1 M HClO₄ aqueous solutions with 0.01, 1 and 10 mM H₂SQ concentrations (panels A, B and C in Figure 6, respectively). The spectra collected in the 0.01 mM solution in potential step experiments show, for potentials between 0.30 and 0.90 V, positive bands at 1490-1504 and 1760-1770 cm⁻¹ for adsorbates coming from squaric acid. These features are accompanied by a positive feature at ca. 1110 cm⁻¹, that can be related to coadsorbed perchlorate anions⁷², and a negative band at 1616 cm⁻¹ related to displaced weakly hydrogen-bonded water molecules⁷². A negative-going band appears also for the corresponding O-H stretching modes of water at ca.

3480 cm^{-1} (not shown). The intensity of these bands steadily increases with the electrode potential up to 0.90 V, with the band frequencies of the positive features being shifted to higher values. For H_2SQ concentrations higher than 0.01 mM, it can be observed that, except for the perchlorate bands, the intensity of the positive bands at a given electrode potential increases for higher H_2SQ concentrations, with their band frequency at a given electrode potential being shifted to higher wavenumbers. This behavior confirms the relation between the bands at ca. 1490-1504 and 1760-1770 cm^{-1} with adsorbed species coming from H_2SQ . These adsorbates, that can be detected in ATR-SEIRAS experiments at much lower H_2SQ concentrations than in the case of IRRAS, due to a higher surface sensitivity, prevail at the electrode surface to the detriment of adsorbed perchlorate anions when squaric acid concentration is high enough. Note that the band for adsorbed perchlorate at ca. 1100 cm^{-1} is not observed clearly in the IRRA spectra shown in Figure 2 due to the cutoff of the CaF_2 window.

Figure 6. Potential-difference ATR-SEIRA spectra collected during potential step experiments with a Au(111)-25 nm thin film electrode in a x mM H_2SQ + 0.1 M HClO_4 solution prepared in water (A-C) or in D_2O (D). x= A) 0.01; B) 1; C-D) 10. The reference spectrum was collected at 0.10 V in the same solution. 100 interferograms were coadded at each potential with a 8 cm^{-1} spectral resolution.

For the 1 mM H₂SQ solution (Figure 6B), an additional positive feature is observed at ca. 1640 cm⁻¹ which is better observed for the 10 mM solution (Figure 6C). This new band could be assigned in a first approach to the strongly hydrogen bonded water molecules characteristic of the gold/solution interface for potentials above the potential of zero charge⁷². However, this latter assignment would involve the observation of a positive band in the OH stretching region between 3200 and 3600 cm⁻¹ (superimposed to the negative contribution for displaced water molecules at ca. 3480 cm⁻¹) that is not observed at potentials below 0.90 V (see ³⁸ and results reported below for potential scan experiments).

In order to decide on the origin of the band at ca. 1640 cm⁻¹, additional experiments were carried out in solutions prepared in deuterium oxide. Under these conditions, eventual contributions from the bending mode of water molecules are expected to be shifted to ca. 1200 cm⁻¹. The spectra collected in D₂O for the 10 mM H₂SQ solution are reported in Figure 6D. Spectra for the 0.01 and 1 mM H₂SQ solutions are provided as supplementary information (Figure S1). The spectra obtained in deuterium oxide solutions show a negative band at ca. 1200 cm⁻¹ associated to the OD bending of D₂O molecules instead of the feature at ca. 1616 cm⁻¹ typical of the spectra in water (see Figures 6 A to C). The rest of bands in the spectra collected in deuterium oxide H₂SQ-containing solutions are similar to those observed in water solutions for the same H₂SQ concentration, with just minor shifts to lower wavenumbers in the deuterium oxide solution. This includes the positive band at ca. 1630-1640 cm⁻¹ that, in consequence, can be related also to species coming from squaric acid and not to the solvent. Besides, and assuming the existence of full hydrogen-deuterium exchange for H₂SQ and HSQ species in the deuterium oxide solution, it can be concluded from the experimental spectra that bands related to adsorbed species coming from squaric acid should have, if any, only a small contribution from hydrogen (or deuterium) atoms. This conclusion is consistent with the assignments of the observed bands at ca. 1550 and 1770 cm⁻¹ to adsorbed SQ (no H/D atoms and, thus, no effect of replacing water by D₂O in the spectroelectrochemical experiments). As previously discussed for the IRRA spectra (see above), the absence in the ATR-SEIRA spectra of experimental features at ca. 1820, 1416 and 1302 cm⁻¹ (with the last two bands eventually shifting to lower band frequencies upon deuteration) seems to preclude the existence of adsorbed H₂SQ. In this respect, it has to be noted that the absence of features at ca. 1208 and 1108 cm⁻¹, for the out-of-phase $\delta(\text{C-OH})$ and $\delta(\text{C-OD})$ bending modes (see Table 2), in the spectra collected in water and D₂O, respectively, is not a so good criterion for deciding on the presence of H₂SQ due to interferences from the silicon substrate and co-adsorbed perchlorate anions. Regarding the eventual coexistence of bisquarate and squarate anions at the gold surface, the former could contribute to the feature at ca. 1770 cm⁻¹ and thus explain the observation of the band at ca. 1630 cm⁻¹ (see Table 3). However, and according to DFT calculations, the presence of significant amounts of adsorbed

HSQ should imply the observation of bands at ca. 1440 (shifting slightly downwards for DSQ) and 1309 cm^{-1} (moving down to 1209 cm^{-1} for DSQ). A feature at ca. 1068 cm^{-1} for HSQ would overlap with perchlorate contributions.

From the absence of clear bands in the spectral range between 1450-1250 cm^{-1} in Figures 3 and 6, it can be preliminarily concluded that the feature at ca. 1630 cm^{-1} is not related to the presence of adsorbed HSQ. Thus, an alternative origin for this band should be given. This can be done on the basis of the DFT calculations for the harmonic frequencies of adsorbed squarate at different coverages. According to the data reported in Tables 4 and 5, the existence of significant portions of the surface having high-density domains of adsorbed squarate would give rise to collective modes that could be at the origin of a coverage-driven strong frequency shift predicted from the theoretical calculations. As follows from the calculated frequencies, the symmetric $\text{O}_{\text{ad}}\text{CC}_{\text{ad}}\text{O}$ stretch mode would appear around 1550-1560 cm^{-1} for low coverages at Au(111) surfaces, but for high coverages would split into a component around 1630 cm^{-1} , due to the in-phase collective mode, and a lower wavenumber feature (around 1540 cm^{-1}) due to the out-of-phase collective motion of the dipoles. As mentioned above, a similar splitting (but with a less important frequency shift) is observed in the calculated frequencies for the uncoordinated OCCO stretching mode (from 1762 cm^{-1} for $\Theta=1/9$ from 1790-1714 cm^{-1} for $\Theta=1/3$). A similar behavior can be deduced from the inspection of the data in table 5 for Au(100). Thus, the existence of segregated domains with distinct local squarate coverages could explain the broadening of the experimental bands which is much clearer in the ATR-SEIRA than in the IRRAS spectra. Figure S2 shows a tentative deconvolution (in Gaussian components) of the vibrational band at 1500-1550 cm^{-1} for several of the ATR-SEIRA spectra reported in Figure 6D. It is clear from this figure the existence of several contributions, whose relative intensities change when the electrode potential (and, thus, the adsorbate coverage) is increased. This behavior is paralleled by the development of the band at 1627-1630 cm^{-1} (see Figure 6D), that is not observed at lower potentials (and coverages), in agreement with its absence in the calculations for the lower coverages studied. All these results suggest the coexistence at the gold electrodes in contact with squaric acid solutions of local domains with different squarate coverages giving rise to the overlapping contributions in the observed infrared adsorbate bands. The observation of contributions around or slightly below 1500 cm^{-1} (see also the spectra in Figures 6 A and B) would suggest the existence of surface domains with lower adsorbate coverages. Calculations for SQ adlayers with coverages as low as 1/16 yield harmonic frequencies that still are significantly higher than those recorded in the experiments.

The latter arguments can thus be used to propose assignments for the experimental bands observed in both IRRAS and ATR-SEIRA spectra that are summarized in Table 6. Note that, other than the bands for carbon dioxide and related adsorbed bicarbonate species, all the

adsorbate bands between 1800 and 1450 cm^{-1} can be related to adsorbed squarate anions. It must be kept in mind that the actual picture of the adsorbed adlayers can be much more complicated than the simplified models used in the DFT calculations reported in this work, with an eventual coadsorption of bisquarate and squarate species that could also interact with interfacial water with the formation of hydrogen bonds. These hydrogen bonds probably have some influence on the vibrational frequencies, because of modifications in the adsorbate-adsorbate interactions, and in the patterns of dipole coupling. The previous effects can be invoked, in particular the formation of hydrogen bonds that would involve some negative charge density from the oxygen atoms of the studied adsorbates, probably leading to some weakening of the C-O bond orders, to explain that the experimental values of the deconvoluted experimental bands in the range 1500-1580 cm^{-1} are systematically downshifted with respect to the calculated harmonic vibrational frequencies reported in this paper. Part of the discrepancy can also be due to computational errors due to the choice of the functional. An analysis of the relative importance of these factors would need a significant amount of computational work and are out of the scope of this paper.

Table 6. Vibrational band assignment for the experimental bands recorded in IRRAS (Figure 3) and ATR-SEIRAS (Figure 6).

Experimental frequency / cm^{-1}	Assignment
2343	CO_2 (in solution)
1750-1810	Sym OCCO stretch (adsorbed SQ)
1620-1660	Sym OadCCOad stretch (collective in-phase vibration, at medium-high coverages of adsorbed SQ)
1500-1550	Sym OadCCOad stretch (at low SQ coverages) Sym OadCCOad stretch (collective out-of-phase vibration, at medium-high coverages of adsorbed SQ)
1415-1425	HCO_3^- (adsorbed)

Note: asymmetric OCCO and OadCCOad modes would not be observable as a consequence of the surface selection rule.

Figure 7. Potential-difference ATR-SEIRA spectra collected during a potential scan experiment with a Au(111)-25 nm thin film electrode in a 10 mM H₂SQ + 0.1 M HClO₄ solution prepared in water. The reference spectrum was collected at 0.10 V in the same solution. 104 interferograms were coadded at each potential with a 8 cm⁻¹ spectral resolution.

Figure 7 shows the ATR-SEIRA spectra obtained in an additional experiment in which the electrode potential was scanned at 2 mV·s⁻¹ from 0.10 to 1.70 V in the 10 mM H₂SQ solution. Spectral bands at 1760-1775, 1635 and 1490-1550 cm⁻¹ for potentials below 1.00 V are similar to those reported in Figure 6C. The spectra in Figure 7 show clearly that the positive band at ca. 1635 cm⁻¹ is decoupled from the water stretching features which appear as a broad negative band at ca. 3480 cm⁻¹. Additional positive bands appear for potentials above 1.10 V at ca. 1111 and 1390-1415 cm⁻¹ accompanied by a small band at ca. 2343 cm⁻¹ and a band at 3601 cm⁻¹ in the OH stretching region. The potential-dependent behavior of the band intensity and band frequency of some of these features is reported as in Figure 4C together with data from a similar experiments carried out in a 0.01 M H₂SQ solution in water. The plots for the band at ca. 1630 cm⁻¹ correspond to the spectra collected in a 10 mM H₂SQ solution in D₂O. In general, the

observed changes in band frequencies and intensities in the 10 mM H₂SQ solution are similar to those described above for gold single crystal electrodes (see Figures 4A and B). Regarding the effect of squaric acid concentration, it is clear that bands for squaric acid-related species are more intense and appear at lower electrode potential for the higher H₂SQ concentration. Finally, it can be remarked from Figures 7 and 4C that the new features for potentials above 1.10 V are related to the oxidative removal of the adsorbates coming from H₂SQ. Namely, the small feature at 2343 cm⁻¹ corresponds to dissolved carbon dioxide, which is difficult to detect in the ATR-SEIRA spectra because the produced molecules are not retained close to the electrode surface as in external reflection experiments. As previously observed in the ATR-SEIRA spectra collected during the oxidation of other organic molecules such as oxalic acid⁷³, the formation of adsorbed bicarbonate in equilibrium with carbon dioxide can be easily detected from the corresponding band at 1415 cm⁻¹ giving rise, in the present case, to a well-defined feature in the spectra between 1.10 and 1.60 V. Adsorbed bicarbonate competes with perchlorate anions, which, as witnessed by the development of the positive band at ca. 1110 cm⁻¹, adsorbs at the gold electrode once the squaric acid-related adsorbates are oxidatively stripped. Note that the spectrum obtained at 1.30 V is similar to that observed in H₂SQ-free perchloric acid solutions, including the positive-going feature at ca. 3601 cm⁻¹⁷².

5. Conclusions

A study of the adsorption and reactivity of squaric acid and related species at gold electrodes has been carried out. The combination of spectroelectrochemical techniques (ATR-SEIRAS or IRRAS and cyclic voltammetry) and DFT calculations of adsorption geometries and theoretical harmonic frequencies has provided new insight regarding the nature of the species responsible for the experimentally observed IR bands. In this respect, we can discard the non-dissociated squaric acid species, as its interaction with the gold surface is very weak (as evidenced by the long Au-O calculated distances, typical of physisorbed systems). On the basis of the observed experimental band frequencies, and the calculated adsorbate geometry and vibrational frequencies, adsorbed squarate (SQ) species are present at the surface at significant coverages. As found for some carboxylic acids⁷³⁻⁷⁶ and carbon dioxide⁷¹, the presence of adsorbed anions, in solutions where a more acidic form (squaric acid or bisquarate anions in the present case) is the main species, reflects the existence of a deprotonation step upon adsorption.

Significant broadening and the presence of shoulders have been evidenced in the experimental spectra, especially for the higher concentrations in the ATR experiments. Theoretical calculations have shown strong coverage effects on the harmonic frequency values for squarate

adlayers that arise from the transition dipole coupling due to collective adsorbate vibrational modes with different degrees of dephasing. This provides a natural explanation to the significant broadening of the experimental bands and to the appearance of multiple maxima and/or shoulders observed in the experimental spectra, including the band at 1630 cm^{-1} , without need of invoking the presence of new adsorbates (namely, adsorbed bisquarate) or different adsorption geometries. Some significant difference exists between the values of the calculated frequencies for the experimentally observable bands and those recorded in the experiment. Besides the errors intrinsic to the DFT calculation, in particular the choice of the functional, most of this frequency discrepancy is expected to be due to interactions between the species present at the electrified interface, in particular the formation of hydrogen bonds between the SQ adsorbates with interfacial water molecules.

Regarding the sensitivity of the vibrational frequencies of the adsorbate versus crystallographic orientations of the Au(111) and Au(100) electrode surfaces, no significant differences have been found neither in the experimental nor in the harmonic frequencies resulting from the DFT calculations. Experimentally, a stronger adsorption of squarate at the Au(100) electrode can be suggested from the observation of the corresponding bands at lower potentials compared to Au(111).

Electrochemical oxidation of squaric acid proceeds with the formation of carbon dioxide as the main oxidation product at gold electrodes with no other detected adsorbed oxidation product other than bicarbonate anions, which is formed from the carbon dioxide molecules existing at the vicinity of the electrode surface.

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Supporting information

Potential-difference ATR-SEIRAS spectra for Au(111)-25nm electrodes at various squaric acid concentrations in acidic deuterium oxide solutions and tentative deconvolution of the bands observed in those spectra between 1400 and 1600 cm^{-1} .

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