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Cyanate and Cyanurate Adsorption at Silver Electrodes in Neutral Solutions. In Situ ATR-SEIRAS and DFT Studies

William Cheuquepán¹, Antonio Rodes^{2,3}, José M. Orts^{*2,3,#}

²Departamento de Química Física and ³Instituto Universitario de Electroquímica
Universidad de Alicante, Apartado 99, 03080 Alicante, SPAIN

¹Present address: Departamento de Química, Universidad de Burgos
Pza. Misael Bañuelos s/n, 09001 Burgos, SPAIN

#Corresponding author. E-mail: jm.orts@ua.es

Abstract

The adsorption and reactivity of cyanate at silver electrodes is studied spectroelectrochemically in sodium perchlorate solutions and compared to those of cyanuric acid (1,3,5-triazine-2,4,6-trione, C₃H₃N₃O₃). The Surface Enhanced Infrared Reflection Absorption spectra obtained under Attenuated Total Reflection conditions (ATR-SEIRAS) for low cyanate concentrations show that some amount of adsorbed CO is formed at the silver electrode surface at low electrode potentials. Adsorbed cyanate species are formed at higher potentials and predominate at the electrode surface. However, for cyanate concentrations above 1 mM, the ATR-SEIRA spectra show potential-dependent absorption features between 1800 and 1300 cm⁻¹, which are similar to those obtained after dosing cyanuric acid to the sodium perchlorate solution. This observation suggests that adsorbed cyanuric acid-related species are formed from cyanate anions at the silver surface sites as the result of an electroless trimerization reaction. The infrared spectra collected in the cyanuric acid-containing solutions also show a higher amount of adsorbed CO at low potential when compared to that observed in cyanate-containing solutions, thus indicating certain instability of cyanuric acid at the silver surfaces. Density Functional Theory (DFT) calculations have allowed the study of the effect of crystallographic orientation and bonding geometry on the adsorption energy and vibrational frequencies of adsorbates. Also, the effect of adsorbate coverage on the vibrational frequencies has been investigated. In the case of cyanate, DFT calculations show that the most favourable adspecies is N-bonded cyanate adsorbed in fourfold-hollow (100) sites. The experimental spectra in cyanuric acid solutions agree with the formation of adlayers of specifically adsorbed triketo-monocyanurate species that adsorb, in a tridentate configuration, perpendicular to the electrode surface. The polyoriented nature of the silver surface

used in the spectroelectrochemical experiments, together with the eventual existence of cyanate in domains with different local coverages, can explain the broadness of the band for the asymmetric OCN stretching. For adsorbed triketo-monocyanurate, high local coverages are at the origin of the band observed experimentally at ca 1790 cm⁻¹ that can be associated to the in-phase collective CO stretching.

1. Introduction

Cyanate is a simple model anion whose adsorption and reactivity at different metal electrodes have attracted the interest of different research groups in the past.¹⁻¹¹ This interest is partially related to the reported formation of adsorbed cyanate as a product of the electrochemical oxidation of several related substances such as cyanide,^{4,12} thiocyanate¹³ and semicarbazide.¹⁴ For aminoacids, such as glycine¹⁵⁻²⁰ or L-serine^{19,21-23}, the same feature observed around 2100 cm⁻¹ in the infrared spectra during their electrochemical oxidation has been tentatively assigned either to adsorbed cyanate^{17,20} or to adsorbed cyanide.^{15,16,18,19,22,23} In addition to the similarity between the band frequencies for these adsorbates, the formation of adsorbed cyanate upon oxidation of adsorbed cyanide has to be taken into account to understand these discrepancies.^{4,12} It is also noteworthy that adsorbed cyanate species has been spectroscopically detected as a product of the reactions in the gas phase between CO and NO at various metals.²⁴⁻²⁸

The spectroscopic characterization of the adsorbed adlayers formed at metal electrode surfaces in cyanate-containing solutions has been carried out mainly with in situ infrared¹⁻¹¹ and Raman^{3,8} spectroscopies. The corresponding spectra showed features in the range 2100-2250 cm⁻¹, which were commonly assigned to the asymmetric stretch of N-bonded adsorbed cyanate. Some authors suggested that the spectroscopic features observed at higher wavenumbers in the latter range were due to the formation of adsorbed isocyanic acid.^{4,6}

In a more recent paper, our group explored the adsorption of cyanate at gold single crystal electrodes combining cyclic voltammetry and in situ external reflection infrared spectroscopy measurements with periodic Density Functional Theory (DFT) calculations.²⁹ In that work, the nature of the adsorbed species, their bonding geometry and adsorption sites were investigated as well as the effect of adsorbate coverage on the observed spectra. From DFT results, it was concluded that neither isocyanic nor cyanic acids adsorbates were responsible for any of the observed bands in the infrared spectra. Also, it was shown that N-bonded cyanate is much more stable than the O-bonded species. Besides, DFT calculations for adlayers with different coverages have shown that some splitting of the vibrational bands arises as a consequence of the existence of in- and out-of-phase collective vibrations at high and intermediate coverages.²⁹

The spectroscopic study of adsorbed species formed from cyanate-containing solutions was later extended to gold thin film electrodes.^{30,31} This allows the collection of spectra under Attenuated Total Reflection (ATR) conditions with a much better sensitivity associated to the Surface Enhanced Infrared Absorption (SEIRA) effect.^{32,33} Controlled deposition conditions of the gold thin layer lead to preferentially (111)-oriented gold surfaces³³⁻³⁵ whose behavior can be compared to that of Au(111) electrodes. Under these experimental conditions, the ATR-SEIRA spectra showed new features, not observed in the external reflection experiments with gold single crystal electrodes, suggesting the presence of other adsorbates formed from adsorbed cyanate. These features were similar to those observed in solutions containing cyanuric acid (1,3,5-triazine-2,4,6-trione, $C_3H_3N_3O_3$),^{30,31} which is a stable cyclic trimer of isocyanic acid (HNCO).³⁶ From its pK_a values (6.88, 11.40 and 13.55),³⁷ only the undissociated acid and the cyanurate monoanion would have a significant concentration in neutral solutions. The adsorption of cyanuric acid or the monocyanurate anion was strongly suggested by the observation of intense bands in the typical carbonyl region between 1800 and 1700 cm^{-1} .^{30,31} DFT calculations indicated that the most stable adsorbed form of the undissociated cyanuric acid is the triketo form, which lies parallel to the gold surface, in such a way that in-plane vibrations would not be infrared active according to the surface selection rule.^{38,39} Focusing on monocyanurate species, it was found that the triketo tautomer, with three atoms (O-N-O) bound to the metal at on-top positions and with the molecular plane perpendicular to the metal surface, is the most stable species when compared to enolized species.

The aim of this paper is to extend to silver thin films our previous studies for cyanate adsorption and reactivity at gold electrodes. ATR-SEIRAS spectra have been collected in cyanate- and cyanuric acid-containing solutions for silver thin film electrodes chemically deposited at germanium substrates. These spectra will be interpreted on the basis of DFT calculations for adsorbed cyanate and monocyanurate species. The stability of these species will be discussed as a function of crystallographic orientation (Ag(111) and Ag(100)), bonding geometry (top, bridge or hollow) and adsorbate coverage.

2. Experimental

Voltammetric and in situ infrared experiments were carried out in a 0.1 M $NaClO_4$ solution prepared from $NaClO_4$ (99.99%, Sigma Aldrich) and ultrapure (18.2 $M\Omega\ cm$) water (Elga-Vivendi) to which either sodium cyanate (96% Sigma Aldrich) or cyanuric acid (1,3,5-triazine-2,4,6-trione, $C_3H_3N_3O_3$, 97%, Acros Organics) was added to reach the desired concentration. In these experiments a saturated silver/silver chloride connected to the glass

(spectro)electrochemical cell through a Luggin tube was employed as reference electrode. The counter electrode was a coiled gold wire.

In voltammetric experiments a silver bead grown by melting a 0.5 mm dia silver wire (Alfa Aesar, 99.9985% purity) was used as the working electrode. The surface treatment before each experiment is described in detail in reference ⁴⁰ and involved a chemical polishing step in a mixture of CrO₃ and HCl.⁴¹

The samples used for in-situ infrared spectroscopy experiments were silver thin films deposited on one of the faces of a 32 mm x 32 mm x 32 mm prism of Ge beveled at 60° (EKSMA, Lithuania). The silver thin films were obtained by chemical deposition using the method described in ref.⁴² Briefly, the Ge substrate was immersed in a solution formed by a mixture of 25 μL of a 0.02 M hydrazine solution with 5 mL of a 0.01 M silver nitrate solution containing ammonium hydroxide (0.46 M) and EDTA (0.14 M) ^{43,44} (all chemicals ‘pro analysi’ quality from Merck). Under these conditions, a bright thin silver film is formed. After the desired deposition time, the sample is removed from the silver-containing solution, rinsed with plenty of ultrapure water and dried in an argon (N50) stream. In this work, deposition time was 2,5 min.

Infrared experiments were carried out with Thermo Nexus 8700 and 6700 spectrometers both equipped with a narrow-band nitrogen-cooled MCT detector and an Al-grid ZnSe polarizer. The spectroelectrochemical cell was placed at the top of a variable-angle Veemax (Pike Technologies) reflectance accessory. The ATR-SEIRA spectra were collected with p-polarized light and an incidence angle of 60°. All spectra were collected with a resolution of 8 cm⁻¹ and are represented as $-\log(R/R_0)$, where R and R₀ stand for the sample and reference single beam reflectance spectra, respectively.

The spectroelectrochemical cell is a modification of the cell employed in external reflection experiments. ⁴³ The cell is provided with a Ge window onto which a silver thin film, which acts as the working electrode, is deposited as described above. Electric contact with the silver film is achieved with a thin gold foil. A saturated silver/silver chloride electrode and a gold foil were used as reference and counter electrodes, respectively. The cleanliness of the surface of the thin-film silver electrode was checked from both the cyclic voltammogram and the potential-dependent ATR-SEIRA spectra recorded in the sodium perchlorate solution.

3. Computational details

DFT calculations were carried out using the Vienna Ab-Initio Simulation Program (VASP, version 4.6) code ⁴⁵⁻⁴⁸, for obtaining optimized geometries and harmonic vibrational frequencies

of cyanate and monocyanurate species adsorbed on model Ag(100) and Ag(111) surfaces. In all calculations we used the Projector-Augmented-Wave method,^{49,50} with the Generalized Gradient Approximation (GGA) functional of Perdew, Burke and Ernzerhof (PBE)^{51,52} and a cutoff energy of 400 eV for the plane-wave basis set.

The periodic models for the unreconstructed, non-relaxed, Ag(111) and Ag(100) surfaces consisted of (3x3) simulation cells formed by 4 metallic layers (9 atoms each), for a total of 36 metal atoms. In addition, we also used a Ag(111)-(4x4) slab for the study of coverage effects. The slab replicas were separated by a vacuum region of more than 1.2 nm, that ensures that no significant coupling exists between periodic replicas in the Z-direction. The metal nuclei coordinates were kept fixed, with a lattice constant of 0.41470 nm (nearest-neighbor distances of 0.29324 nm). This value, obtained from a series of bulk energy calculations with different lattice constants, and fitting to the Murnaghan equation of state, coincides with the values reported by other authors using the PBE functional, and compares well with the experimental value of 0.4065 nm for pure silver.⁵³

Calculations of systems including metallic slabs used the automatic Monkhorst-Pack⁵⁴ (5x5x1) scheme, for sampling the Brillouin zone. Methfessel-Paxton⁵⁵ smearing was used with $\sigma=0.2$ eV. The convergence criteria were: 10^{-6} eV for the electronic energy, and forces on atoms below 0.02 eV/Angstrom, for the geometry optimization (without restrictions) of the molecular adspecies. The calculated vibrational frequencies were obtained using the harmonic approximation, with atomic displacements of 0.015 Angstrom. 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 almost negligible.

In the case of gas-phase molecular systems, the simulation cell was a cubic box (20 Angstrom side length) containing a single molecular species. Integration in the Brillouin zone only used the gamma point. Smearing choice was Gaussian (with $\sigma=0.1$ eV). As convergence criteria for the free molecular species we chose 10^{-6} eV for the electronic energy, and forces on atoms below 0.002 eV/Angstrom, for the geometry optimization. For the gas phase OCN radical, all the results reported correspond to spin-polarized calculations. All other calculations have been carried out without spin polarization.

Adsorption energies were calculated as the difference between the adsorbate-metal energy and the energies of the gas phase cyanate radical and the adsorbate-free metal slab. Unless otherwise stated, all the energy values reported correspond to electronic energy, without including the zero-point energy (ZPE) correction, as we have verified that the vibrational energy contribution is very

small (about 1% of the adsorption energy values without correction). The visualization of the molecular optimized geometries and vibrational modes has been done using Molden⁵⁶ and Jmol.⁵⁷

4. Experimental results

Figure 1 shows cyclic voltammograms obtained with a silver bead electrode in 0.1 M NaClO₄ solutions containing potassium cyanate with concentrations ranging from 0 to 10 mM. Curve a corresponds to the cyanate-free solution and shows the typical voltammetric profile associated to an almost-constant differential capacity value in the range of stability of both the silver electrode and the solvent. Voltammetric curves recorded in the presence of cyanate show increasing current densities in the potential range between -0.5 and 0.25 V when cyanate concentration is increased. For the 10 mM cyanate solution, a broad quasi-reversible peak can be observed with maxima at ca. 0.0 V.

Figure 1. Cyclic voltammograms from a quasi-spherical silver bead electrode in x mM NaOCN + 0.1 M NaClO₄ solutions with x= 0 (a), 1 (b) and 10 (c). Scan rate 0.100 V·s⁻¹. The inset shows the voltammograms recorded for the same cyanate concentration with the thin film silver electrodes used in the ATR-SEIRAS experiments. In this case, sweep rate was 0.050 V·s⁻¹.

Voltammetric experiments were also carried out with the silver thin film electrodes used in the ATR-SEIRA experiments. These electrodes were chemically deposited on germanium substrates. The limited stability of the latter material determines the available potential range in these experiments, which were limited to potentials below -0.30 V. Some voltammograms obtained in the cyanate containing solution in this potential range are depicted in the inset of Figure 1. As in the case of the silver bead electrodes, the presence of cyanate in the working solution gives rise to almost symmetric features for potentials below -0.50 V. Irreversible oxidation processes can be detected for less negative potentials in the case of cyanate concentrations equal to or higher than 1 mM. It cannot be discarded that this behavior could be related to the reactivity of the germanium substrate.

Prior to the spectroelectrochemical study of the electrode processes taking place in the presence of cyanate anions, the ATR-SEIRA spectra collected for the silver thin film electrode in cyanate-free sodium perchlorate solution have been analyzed to monitor the silver/solution interface. These spectra (Figure S1) show only potential-dependent bands for adsorbed perchlorate anions (band at ca. 1110 cm^{-1}) and displaced interfacial water molecules (negative bands at ca. 1610 and 3500 cm^{-1} for the OH bending and stretching modes, respectively).⁵⁸ These observations can be related to the cleanliness of the silver/solution interface which was achieved for the as-prepared silver electrode after a few potential excursions in the indicated potential range followed by several replacements of the working solution.

Figure 2. Time (A,C) or potential (B) dependent ATR-SEIRA spectra collected for a silver thin film electrode in x mM NaOCN + 0.1 M NaClO₄ solutions with x = 0.01 (A,B and lower part of C (0-10 min)) and 0.1 (upper part of C). The arrow indicates the dosing of cyanate at -0.26 V to

reach the 0.1 mM concentration. 100 interferograms collected at each potential. The reference spectrum was collected at -0.91 V both in the cyanate-free 0.1 M NaClO₄ solution (A) and in the 0.01 mMNaOCN + 0.1 M NaClO₄ solution (B,C).

Figure 2A shows a set of time-dependent ATR-SEIRA spectra collected at -0.91 V after the dosing of sodium cyanate (to reach a 0.01 mM concentration) in the spectroelectrochemical cell. These spectra are referred to the single beam spectrum obtained at the same electrode potential just before dosing. The resulting absorbance spectra show positive bands at ca. 3450 and 1610 cm⁻¹ that can be ascribed to the O-H stretching and bending bands of interfacial water molecules. According to the positive sign of these features, water molecules seem to be incorporated at the silver-solution interface. This process is paralleled by the development of a small feature at 1982 cm⁻¹. As a first approach, we can remark here that the observed band frequency does not fit with that of the features observed between 2100 and 2200 cm⁻¹ for adsorbed cyanate at gold²⁹⁻³¹ and silver electrodes (see below). In fact, no band is observed in Figure 2A in this latter spectral range. On the other hand, the band at ca. 1982 cm⁻¹ lies in the same frequency region as the C-O stretching mode of adsorbed CO (see section 5.3). Once the time-dependent spectra obtained in the experiment reported in Figure 2A reached a stationary behavior, the electrode potential was stepped to less negative values up to -0.26 V in the 0.01 mM cyanate solution. The spectra obtained under these conditions at several electrode potentials, which are referred to that collected at -0.91 V in the 0.01 mM cyanate solution, are depicted in Figure 2B. These spectra show, for potentials below -0.60 V, a bipolar feature centered at ca. 1990 cm⁻¹, which reflects a potential-dependent upward shift of the band observed at ca. 1982 cm⁻¹ in Figure 2A. For potentials above -0.60 V the band becomes negative, witnessing the removal of the species associated to this feature. In fact, the band tentatively assigned to adsorbed CO is replaced by a well-marked positive band at ca. 2156 cm⁻¹ that can be related to the adsorption of cyanate anions as this band frequency is similar to that observed for these species on several metal electrodes,^{1-11,29} including silver,² in cyanate solutions. Besides, a strong band at ca. 1100 cm⁻¹ can be related to the potential-dependent co-adsorption of perchlorate anions whereas a negative band at ca. 1610 cm⁻¹ can be linked to the displacement of interfacial water molecules.

The experiment reported in Figures 2A and B was completed by polarizing the electrode potential at -0.26 V in the 0.01 mM cyanate solution. A series of time-dependent spectra collected under these conditions (lower spectra in Figure 2C) show that, for short polarization times, the intensities of the bands described in Figure 2B decrease slightly. This behavior is paralleled by the observation of increasing band intensities for interfacial water and coadsorbed perchlorate features. Then, an additional amount of the cyanate salt was added in the working solution (to reach a concentration of 0.10 mM). The spectra recorded subsequently (which are referred to that

collected at -0.26 V in the 0.01 mM cyanate solution) show a sudden increase of the band at ca. 2150 cm^{-1} that first shifts up to 2170 cm^{-1} and later undergoes a decrease of its band intensity and band frequency (down to 2167 cm^{-1}). This behavior parallels the development of new spectral features at ca. 1789, 1724, 1446, 1388 and 1319 cm^{-1} . A negative-going band at ca. 1100 cm^{-1} reflects the displacement of coadsorbed perchlorate anions. At this point, it is not clear whether the positive-going band at ca. 1643 cm^{-1} in Figure 2C is related to the OH bending mode of incorporated interfacial water molecules or to the same species giving rise to the aforementioned positive bands.

Figure 3. ATR-SEIRA spectra collected for a silver thin film electrode in x mMNaOCN + 0.1 M NaClO₄ solutions with x=0.1 (A), 1 (B) and 10 (C). 100 interferograms collected at each potential. The reference spectrum was collected at -0.91 V in the same working solution.

Figures 3A, B and C show sets of potential-dependent spectra recorded in experiments carried out in the sodium perchlorate solution after dosing sodium cyanate at -0.91 V to reach

concentrations of 0.1, 1.0 and 10 mM, respectively. The reference spectrum for each set of spectra was recorded at -0.91 V after the dosing of each cyanate concentration at this electrode potential. The spectra in Figure 3A show the appearance of a small feature at ca. 2152 cm^{-1} for potentials above -0.41 V which increases and shifts up to 2167 cm^{-1} in the spectra collected at -0.26 V. At this latter potential, other small features can be observed at ca. 1724, 1380 and 1315 cm^{-1} . These latter band frequencies are similar to those of some of the features observed in Figure 2C. As a difference with the experiment corresponding to this latter figure, the potential-dependent perchlorate band in Figure 3A shows a continuous increase from -0.76 V to -0.26 V in agreement with a continuous increase of perchlorate coverage as the electrode potential is made less negative. Besides, a negative-going feature at ca. 1610 cm^{-1} is observed in connection with the potential-dependent displacement of weakly hydrogen-bonded water molecules. Regarding the experiments carried out with the 1.0 and 10 mM cyanate solutions, the corresponding spectra show a potential-dependent band in the range between 2150 and 2180 cm^{-1} and a set of additional bands for frequencies between 1800 and 1300 cm^{-1} . All these features appear at potentials as low as -0.81 V for the 10 mM cyanate solution. In general, the intensity of these features for a given electrode potential is higher for the higher cyanate concentrations, except for the band at ca. 2180 cm^{-1} , which is lower for the 10 mM solution in comparison to that observed for a cyanate concentration of 1 mM. No bands for coadsorbed perchlorate and displaced water molecules can be observed for the 10 mM cyanate solution, suggesting that high coverages of adsorbed species coming from cyanate anions block the electrode surface for perchlorate coadsorption. From the relative intensities of the signals between 1300 and 1700 cm^{-1} , the well-marked positive feature at ca 1658 cm^{-1} does not seem to be related to interfacial water but to adsorbed species giving rise also to the bands observed at ca. 1793, 1747, 1581, 1442 and 1378 cm^{-1} . A small feature at 1319 cm^{-1} in figure 3B appears as a shoulder of the band at ca. 1378 cm^{-1} in Figure 3C. Note that, except for the band at 1319 cm^{-1} , the observed set of experimental spectral features resemble those observed under similar conditions with gold electrodes and assigned to the formation of adsorbed cyanurate anions.^{30,31}

Figure 4. ATR-SEIRA spectra collected for a silver thin film electrode in x mM $C_3H_3N_3O_3$ + 0.1 M $NaClO_4$ solutions with $x = 0.01$ (A), 0.1 (B) and 10 (C). 100 interferograms collected at each potential. The reference spectrum was collected at -0.91 V in the same working solution.

Spectroelectrochemical experiments have been carried out with the silver thin film electrodes in cyanuric acid-containing solutions in order to confirm the formation of related adsorbates coming from this species and to compare the corresponding spectra with those discussed above for cyanate-containing solutions. In this way, the potential-dependent spectra reported in panels A to C in Figure 4 were collected, respectively, in 0.01, 0.10 and 10 mM sodium cyanurate solutions. Except for the bands at ca. 2150 and 1319 cm^{-1} , which are absent in the potential-dependent spectra reported in Figure 4, positive absorption bands observed in the cyanuric acid-containing solution at 1793, 1757, 1662, 1442 and 1396 cm^{-1} (values for the 10 mM solution). These band frequencies are similar to those described above for Figure 3 in the spectral range below 1800 cm^{-1} . Besides, a similar potential- and concentration-dependent behavior can be appreciated, with the intensity of the observed bands increasing for a given cyanuric acid concentration as the electrode potential increases up to -0.26 V. At the same time, the onset potential for the positive bands is as low as -0.81 V for concentrations equal or higher than 0.1 mM.

As mentioned above, no band for adsorbed cyanate above 2100 cm^{-1} can be observed irrespective of the cyanuric acid concentration. This behavior seems to indicate a remarkable stability of adsorbed cyanurate species. However, it has to be noted the presence of a negative band in the range $1975\text{--}1990\text{ cm}^{-1}$, which is better observed in the upper spectrum in Figure 4C. This feature is similar to that described above for the cyanate solutions (see figure 2) and again lies in the frequency region characteristic of adsorbed CO. The negative sign of this feature suggests that CO is formed at the reference (dosing) potential, being displaced by adsorbed cyanurate for less negative potentials. In order to check this statement, additional experiments were carried out in which time-dependent spectra were collected at -0.91 V just after the dosing of cyanuric acid. The obtained spectra for a 1 mM cyanuric acid concentration (Figure 5A), show a clearly positive feature at ca. 1980 cm^{-1} whose intensity increases with time after dosing. The bipolar feature centered at ca. 1610 cm^{-1} suggests the reorientation of interfacial water molecules whereas the negative band at ca. 1100 cm^{-1} indicates the displacement of coadsorbed perchlorate anions.

The time-dependent spectra obtained after dosing cyanuric acid at potentials above -0.91 V has also been studied in order to check the effect of the dosing potential on the amount of adsorbed CO. In this way, the spectra reported in in figure 5B were collected during a dosing experiment at -0.41 V . These spectra show the same bands at ca. 1793 , 1757 , 1662 , 1442 and 1396 cm^{-1} that are observed at this potential value after dosing at -0.91 V (Figure 5A). This suggests that the surface composition at a given electrode is the same irrespective of the dosing potential. Regarding the eventual formation of adsorbed CO, from the absence of positive bands for this species in the spectra reported in Figure 5B it can be assumed that the latter process is impeded by the high coverage of the species responsible for the observed positive bands. This latter species prevails at the silver electrode surface for high enough potentials. Additional experiments were carried out in which the electrode potential, after dosing cyanuric acid at -0.41 V , was stepped down to -0.91 V and then up to -0.41 V . In comparison with the spectra reported in Figures 4A-C and 5B, the potential-dependent spectra obtained in these experiments (referred to that collected at -0.41 in the cyanuric acid solution) show negative bands at ca. 1793 , 1757 , 1662 , 1442 and 1396 cm^{-1} when going from -0.41 to -0.91 V (not shown). These features, showing the same band frequencies as the bands in figures 4A-C and 5B, disappear when the electrode potential is raised up to -0.41 V . This behavior is related to the potential-dependent changes in the adsorbate coverage (decreasing from -0.41 V to -0.91 V and rising up again from -0.91 to -0.41 V). It is worth mentioning that, for the lower electrode potentials, a small positive feature appears at ca. 1980 cm^{-1} proving again the formation of adsorbed CO when the coverage of adsorbed cyanurate species is low enough.

Figure 5. Time-dependent ATR-SEIRA spectra collected for a silver thin film electrode in 1.0 mM $\text{C}_3\text{H}_3\text{N}_3\text{O}_3$ + 0.1 M NaClO_4 solutions after dosing of cyanuric acid at A) -0.91 V and B) -0.42 V. 100 interferograms collected at each potential. The reference spectrum was collected at the same potential in the cyanuric acid-free 0.1 M NaClO_4 solution.

5. Computational results and discussion

5.1. Adsorption of cyanate on Ag(111) and Ag(100)

In this section we present the results of the DFT calculations carried out to study the adsorption of cyanate on silver surfaces. The samples employed in the spectroelectrochemical experiments reported in this work (chemically deposited thin layers) have to be considered mainly as polycrystalline because of the preparation conditions,^{43,44} which lead to a relatively fast deposition process. We studied cyanate adsorption on Ag(111) and Ag(100) in order to assess the effect of the surface crystallographic orientation and bonding geometry on the adsorption energy and intramolecular vibrational modes of adsorbed cyanate. First, we will compare the relative stability of N-bonded and O-bonded cyanate species. Then, effect of cyanate coverage on the vibrational frequencies will be discussed. We consider, as a reference, the case of Ag(100)-(3x3)-NCO and Ag(111)-(3x3)-NCO structures corresponding to a surface coverage of $\Theta=1/9$.

In order to know about the relative stability of the different bonding modes of cyanate on Ag(111) and Ag(100) surfaces, we studied the adsorption of N-bonded cyanate on top, bridge, and hollow sites. N-bonding was found to be much more favorable than O-bonding from DFT calculations.²⁹ Nevertheless, we have checked the relative stability of N- and O-bonded cyanate

configurations on the Ag(111) surface. The calculated energy data for the Ag(hkl)-(3x3)-NCO systems are summarized in Figure 6 and Table 1.

Table 1. Calculated adsorption energies (in $\text{kJ}\cdot\text{mol}^{-1}$) for cyanate on Ag(100) and Ag(111) surfaces.

	N-down Ag(100)-(3x3)-NCO	N-down Ag(111)-(3x3)-NCO	O-down Ag(111)-(3x3)-NCO
Hollow	-266	-256	-151
Bridge	-262	-249	-148
Top	-231	-217	-122

From the data for Ag(111) in Table 1, we can conclude that, as previously reported for Au surfaces,²⁹ the bonding of cyanate to the metal through the nitrogen atom (N-down configuration) is much more favourable than using the oxygen atom (O-down configuration), by around $100 \text{ kJ}\cdot\text{mol}^{-1}$. This makes unnecessary the calculations for the O-down case on the (100) orientation.

Regarding the effects of surface orientation and adsorption geometry (depicted in Figure 6) on the adsorption energy, it can be said that both are significant. Adsorption of cyanate is slightly more favorable on Ag(100) than on Ag(111) surfaces, the additional stabilization being in the range around $10\text{-}14 \text{ kJ}\cdot\text{mol}^{-1}$. On both surface orientations the most favorable adsorption geometry was found for the n-fold hollow site, closely followed by the bridge site. The differences of adsorption energy amount to $7 \text{ kJ}\cdot\text{mol}^{-1}$ and $4 \text{ kJ}\cdot\text{mol}^{-1}$ on Ag(111) and Ag(100) respectively. The latter value is comparable to the average value of thermal energy at room temperature (around $3 \text{ kJ}\cdot\text{mol}^{-1}$), this meaning that some significant population of the bridge site by adsorbed cyanate could take place on the Ag(111) surface, this being more unlikely on Ag(100). Adsorption of cyanate on the top site can be discarded, as it is significantly less stable (by $39 \text{ kJ}\cdot\text{mol}^{-1}$ on Ag(111) and $35 \text{ kJ}\cdot\text{mol}^{-1}$ on Ag(100)) with respect to the hollow site on each surface.

Figure 6. N-down adsorbed cyanate with (A,D) on top, (B,E) bridge and (C,F) hollow adsorption geometries on (A-C) Ag(111) and (D-F) Ag(100) surfaces.

The adsorption energies obtained for N-down cyanate on silver surfaces are lower than those reported from DFT calculations for Pd(100) (around $-280 \text{ kJ}\cdot\text{mol}^{-1}$ ⁵⁹), Ni(100) surface ($-430 \text{ kJ}\cdot\text{mol}^{-1}$ ⁶⁰) or Cu(100) ($-330 \text{ kJ}\cdot\text{mol}^{-1}$ ^{61,62}) surfaces. However, they are significantly higher than for the Au(hkl) surfaces.²⁹ When comparing results obtained for Ag(hkl) and Au(hkl) surfaces, it can be noted that, in this latter case, N-bonded cyanate was also preferred to the O-bonded species both for Au(111) and Au(100) surfaces, being also more stable at Au(100) when compared to Au(111). Regarding the preferred adsorption sites, N-bonded cyanate was found to be more stable at bridge sites at Au(100), whereas differences between the different adsorption sites were in the range of the average thermal energy (ca. $3 \text{ kJ}\cdot\text{mol}^{-1}$ at 298 K), specially in the case of the Au(111) surface.

For all the types of adsorption sites considered, the optimized geometries have the molecular axis perpendicular to the metal surface. This means that, taking into account the surface selection rule^{38,39} the symmetric and asymmetric stretches of cyanate can be both detected using in-situ IR spectroscopy.

Table 2. Calculated harmonic vibrational frequencies in cm^{-1} for adsorbed cyanate on Ag(100) and Ag(111) surfaces.

	N-down		N-down		O-down	
	Ag(100)-(3x3)-NCO		Ag(111)-(3x3)-NCO		Ag(111)-(3x3)-NCO	
	$\nu_{\text{as}}(\text{OCN})$	$\nu_{\text{s}}(\text{OCN})$	$\nu_{\text{as}}(\text{OCN})$	$\nu_{\text{s}}(\text{OCN})$	$\nu_{\text{as}}(\text{OCN})$	$\nu_{\text{s}}(\text{OCN})$
Hollow	2184	1278	2214	1302	2190	1147
Bridge	2197	1295	2216	1311	2184	1212
Top	2240	1334	2241	1335	2200	1136

For all the cases studied, the highest calculated frequency values for the asymmetric OCN stretching were obtained for adsorption on the less stable site, on-top of a surface silver atom (see Table 2). These values range from 2200 cm^{-1} for O-down adsorption on Ag(111) to 2240 and 2241 cm^{-1} for N-down adsorption on Ag(100) and Ag(111) respectively. The frequencies for adsorption on hollow and bridge adsorption sites have significantly lower values (in the range between 2184 and 2216 cm^{-1}). In the case of Ag(111) the frequency for N-bonded hollow and bridge adsorption differ by only 2 cm^{-1} . That difference is slightly higher for O-down cyanate on Ag(111) (6 cm^{-1}), and for for N-down cyanate on Ag(100) (13 cm^{-1}).

The situation is more complex for the symmetric OCN stretching mode. The highest frequencies correspond to the top site for N-down adsorption on Ag(100) (1334 cm^{-1}), and bridge adsorption on the Ag(111) surface (1311 cm^{-1} for N-down, and 1212 cm^{-1} for O-down). The lowest ones correspond to hollow N-down adsorption on Ag(100) (1278 cm^{-1}), and top adsorption on Ag(111) (around 1335 cm^{-1} for both N- and O-down).

From the calculated adsorption energies reported above, N-down adsorption on hollow sites is expected for cyanate adlayers on both Ag(100) and Ag(111) surfaces. This would result in vibrational signals in the region close to 2140 - 2260 cm^{-1} for the asymmetric stretching mode, and around 1270 - 1360 cm^{-1} for the symmetric vibration. It must be recalled that the calculated values could be affected by an error of up to 2%. In general, the calculated values for the asymmetric OCN stretching are similar for silver when compared to gold (for the same adsorption geometry and surface orientation). In the case of the asymmetric mode, differences are somewhat higher, specially for top sites at Ag(111), with a frequency value ca. 200 cm^{-1} below that for Au(111). In this respect, it has to be noted that, as a difference with gold, a band can be observed in the

ATR-SEIRA spectra collected using silver electrodes at ca. 1315-1320 cm^{-1} that fits well with the calculated value. The absence of bands between 1150 and 1300 cm^{-1} in the experimental spectra also confirm the absence of O-bonded cyanate species on Ag(111) as expected from the calculated adsorption energies.

5.2. Effect of coverage on the vibrational frequencies of adsorbed cyanate.

It has been shown in a previous paper²⁹ that the increase in cyanate coverage at a gold surface gives rise to new infrared absorption peaks in the vicinity of those observed for low adsorbate coverages. These new peaks arise as a consequence of the existence of collective vibrational modes in the adsorbate monolayer. The extent of the observed shifts with coverage depends on the particular vibrational mode and on whether the vibrations of neighboring adsorbates proceed all in-phase, or with different degrees of dephasing. The higher frequency values correspond to the cooperative, all-in-phase vibrations of the asymmetric OCN stretching collective mode, while the lower frequencies correspond to some dephasing in their vibrational motions with respect to their neighbors. This coupling-induced vibrational frequency shift has been previously put in evidence in DFT calculations of adsorbed species (see works by the groups of Sautet^{63,64} and Ricart⁶⁵) and would contribute to the broadening of the absorption bands. In order to evaluate the importance of this effect for N-bonded cyanate adlayers on silver electrodes, we carried out calculations of geometry optimization and harmonic vibrational frequencies for ordered cyanate overlayers on Ag(111) model slabs, at different coverage values. The results are summarized in Figure 7 and Table 3. Only selected frequency values of those modes falling in the experimentally accessible wavenumber range are given, namely those corresponding to the asymmetric and symmetric stretchings of the cyanate adsorbate.

Figure 7. Optimized geometries of N-bonded cyanate adlayers at different coverages on model Ag(111) surfaces. A) $\theta = 1/4$; B) $\theta = 1/3$; C) $\theta = 1/2$.

Table 3. Calculated harmonic vibrational frequencies and mode assignments for hollow-N-bonded cyanate adlayers at different coverage on model Ag(111) surfaces.

Ag(111)-(3x3)-NCO $\Theta = 0.11$		Ag(111)-(4x4)-4NCO $\Theta = 0.25$		Ag(111)-(3x3)-3NCO $\Theta = 0.33$		Ag(111)-(4x4)-8NCO $\Theta = 0.50$	
ν/cm^{-1}	Assign.	ν/cm^{-1}	Assign.	ν/cm^{-1}	Assign.	ν/cm^{-1}	Assign.
2214	Asym OCN stretch	2221	Asym OCN str, in-phase	2249	Asym OCN str, in-phase	2289	Asym OCN str, in-phase
		2191 2190 2190	Asym OCN str, oo-phase	2194 2194	Asym OCN str, oo-phase	2250 2215 2215 2215 2179 2179	Asym OCN str, oo-phase
1302	Sym OCN stretch	1319	Sym OCN str, in-phase	1305	Sym OCN str, in-phase	1331	Sym OCN str, in-phase
		1313 1313 1311	Sym OCN str, oo-phase	1304 1304	Sym OCN str, oo-phase	1329 1329 1329 1329 1327 1327	Sym OCN str, oo-phase

The increase in cyanate coverage leads to a significant blueshift of the frequency for the all-in-phase collective mode involving the asymmetric OCN stretch, from 2214 cm^{-1} for $\theta=1/9$ to values as high as 2289 cm^{-1} for $\theta=1/2$. The out-of-phase collective modes have a variety of values, depending on coverage, ranging from a value as high as 2250 cm^{-1} (a mode where all the N-bonded cyanate species in each row are in-phase, while next-neighboring rows are out-of-phase) to values as low as 2179 cm^{-1} , depending on the degree of dephasing among the neighboring molecular vibrations. The broadening of the spectral region where the observation of the asymmetric OCN stretch signals is expected to become more important with increasing coverage, going from around 30 cm^{-1} for $\theta = 0.25$, to 110 cm^{-1} for $\theta = 0.50$. This means that it would be

possible to observe, upon increase in cyanate coverage, new signals that correspond to the asymmetric OCN stretch as a consequence of the development of collective vibrational modes involving dipole coupling between neighbors.

On the other hand, we do not expect any experimentally observable splitting in the region around 1300 cm^{-1} , as the symmetric OCN stretch seems to be much less sensitive to the effect of coverage.

5.3. Calculated optimized geometry and vibrational frequencies of adsorbed monocyanurate anion on Ag(111) surfaces.

In order to provide theoretical harmonic frequencies for adsorbed monocyanurate on the silver electrode surfaces, we have carried out geometry optimization and vibrational frequency DFT calculations. As discussed in detail in a previous paper,³¹ different species could be expected to adsorb from a solution containing cyanuric acid, namely cyanuric acid itself and the monocyanurate anion, as well as those resulting from two further deprotonations. A complete study of all the possibilities (arising from the combination of different deprotonation level, keto-enol tautomerism and surface bonding modes) would be very expensive from a computational point of view, and is out of the scope of this paper. We have restricted our study to the most likely adsorbate configuration, based on previous calculations on gold single crystal surfaces: triketomonocyanurate anion adsorbed in a tridentate configuration, involving one deprotonated N atom and the two O atoms closer to it, all three directly bonded to three nearest neighboring metal atoms in a row.³¹ Figure 8 shows the optimized geometry for this adsorbate configuration. The most relevant feature of the optimized geometry is that the molecular plane is essentially perpendicular to the metal surface.

Figure 8. Optimized structures for adsorbed triketomonocyanurate adsorbed on Ag(111)-(3x3) slabs, at coverages A) 1/9 and B) 1/3.

The calculated frequencies and mode assignments for tridentate adsorbed monocyanurate species on Ag(111) are shown in Table 4. Only the values lying in the observable experimental range are reported. These values correspond to calculations carried out with a periodic Ag(111)-(3x3) cell containing either only one monocyanurate species ($\theta = 1/9$) or three monocyanurate species ($\theta = 1/3$) with all the surface metal atoms bonded to adsorbate species). A first point to consider is whether the vibrational frequencies correspond to infrared active modes in the light of the surface selection rule for ATR-SEIRAS experiments.^{32,39} As in the case of external reflection experiments with metals,³⁸ this requires the dynamic dipole to have a non-zero component normal to the metal surface. As indicated above, the molecular plane of the adsorbed triketomonocyanurate anion is perpendicular to the metal surface. However, the analysis of the infrared active modes is somewhat complicated due to the fact that the calculated frequencies correspond to complex vibrational modes. If we consider only the vibrational motions appearing to be the main contributions to each calculated frequency, it can be stated that the contribution of the C-O stretching of non-coordinated carbonyl group would make the band at 1750 cm^{-1} to be infrared active. The same holds for the symmetric $\text{O}_{\text{ad}}\text{CN}_{\text{ad}}\text{CO}_{\text{ad}}$ stretching regarding the band at

1634 cm^{-1} but not for the corresponding asymmetric stretch and that for the NCN stretching (non metal-coordinated N atoms) regarding the bands at 1558 and 1426 cm^{-1} . However, the vibrational mode assigned to the latter calculated frequency has a contribution from the $\text{N}_{\text{ad}}\text{CN}$ stretching that will contribute with a dynamic dipole moment normal to the electrode surface. In the case of the 1394 cm^{-1} frequency, the contribution of the symmetric $\text{CN}_{\text{ad}}\text{C}$ stretching would make it infrared active. The asymmetric $\text{CN}_{\text{ad}}\text{C}$ mode would not contribute to the activity of the band at 1326 cm^{-1} .

When comparing the calculated and experimental frequency values in Figures 3 and 4 a good agreement is found for most of the features appearing in the range 1800-1350 cm^{-1} in the ATR-SEIRA spectra with the calculated values reported in Table 4. This makes sound their assignment to vibrational modes of adsorbed monocyanurate with the bonding geometry described in Figure 8. Note that the small feature at 1319 cm^{-1} , which is only observed in the cyanate containing solution, can be better related to the symmetric OCN stretching of adsorbed cyanate anions (see above) whose presence in the cyanuric acid solutions can be ruled out from the clearcut absence of the much more intense feature at ca. 2200 cm^{-1} related to the corresponding asymmetric mode for adsorbed cyanate. These conclusions are similar to that derived from the calculated frequencies for monocyanurate and the experimental values in the spectra obtained with gold electrodes both in cyanate and cyanuric acid-containing solutions,^{30,31} except for the assignment of the band at ca. 1319 cm^{-1} (not detected in the corresponding spectra).

The relatively wide range for the experimental band frequency values of a given adsorbate feature for adsorbed monocyanurate anions can be understood taking into account the frequency shifts associated to the existence of various coverages as a function of the electrode potential and the concentration of cyanuric acid (Figure 4) or cyanate anions (Figure 3) in solution. As mentioned above for adsorbed cyanate, the dipole coupling effect between neighboring adsorbates, that gives rise to a splitting of the infrared frequencies. For adsorbed monocyanurate, this is significant for the signals at ca. 1760, 1634 and 1558 cm^{-1} (obtained for $\theta = 1/9$), that undergo a splitting at high coverage ($\theta = 1/3$) into a high-frequency value, corresponding to the all-in-phase collective mode, shifted by around 50 cm^{-1} with respect to the corresponding low-coverage frequency and those for the out-of-phase collective modes. This shift in frequency explains the observation of a separated signal, as the well-defined absorption peak found experimentally around 1790 cm^{-1} .

Table 4. Selected calculated harmonic vibrational frequencies and mode assignments for tridentate adsorbed monocyanurate (CYN) on Ag(111) at $\theta = 1/9$ and $\theta = 1/3$. Experimental values from the ATR-SEIRAS obtained in the cyanate and cyanuric acid solutions are given for comparison.

Experimental		Calculated			
Cyanate solution	Cyanuric Acid solution	Ag(111)-(3x3)-CYN $\Theta = 1/9$		Ag(111)-(3x3)-3CYN $\Theta = 1/3$	
ν / cm^{-1}	ν / cm^{-1}	ν / cm^{-1}	Assignment	ν / cm^{-1}	Assignment
1793	1793	1760	Str CO	1805	All in-phase
1724-1747	1731-1757		+ Bend CNH	1753, 1753	Out-of-phase
1646	1654-1662	1634	SymO _{ad} CN _{ad} CO _{ad} Str + Str CO + Bend CNH	1668	All in-phase
				1636, 1636	Out-of-phase
1581		1558	AsymO _{ad} CN _{ad} CO _{ad} Str + Bend CNH	1590	All in-phase
				1560, 1560	Out-of-phase
1442	1442	1426	Asym NCN str + AsymO _{ad} CN _{ad} CO _{ad} Str + N _{ad} CNstr	1440	All in-phase
				1411, 1411	Out-of-phase
1380-1392	1380-1396	1394	SymO _{ad} CN _{ad} CO _{ad} Str + Bend CNH (scissoring) + N _{ad} CNstr	1413	All in-phase
				1379, 1379	Out-of-phase
		1326	Bend CNH (scissoring) + SymO _{ad} CN _{ad} CO _{ad} Str + CO str + N _{ad} CNstr	1339	All in-phase
				1310, 1310	Out-of-phase
		1323	Bend CNH (rocking) + N _{ad} CNstr + AsymO _{ad} CN _{ad} CO _{ad} Str	1317	All in-phase
				1314, 1314	Out-of-phase

5.4. Reactivity of cyanate and cyanuric species at silver electrodes.

As in the case of gold, the spectroelectrochemical results reported in this work for silver electrodes has pointed out the existence of reversible adsorption-desorption electrode processes involving either cyanate²⁹⁻³¹ or monocyanurate anions^{30,31} in cyanate- and cyanuric acid-containing solutions, respectively. Moreover, the ATR-SEIRA spectra have shown that, as also observed with gold,^{30,31} cyanate anions (in the protonated form, isocyanic acid) can trimerize at silver electrodes to form stable cyanuric acid molecules that are mainly adsorbed as monocyanurate anions (see above).

However, it is shown in this work that some specific surface processes take place at silver electrodes in the presence of cyanate and cyanuric acid. In this way, the ATR-SEIRA spectra obtained during the dosing of potassium cyanate (see Figure 2) and cyanuric acid (see Figure 5) show at low potentials an absorption band at ca. 1980 cm⁻¹ that was tentatively related to the formation of adsorbed CO at the silver electrode under the reported conditions. This statement can be supported by the comparison of the frequency of the observed feature with both calculated and experimental values for CO adsorbed at silver surfaces. In this way, Gajdos et al⁶⁶ obtained, from DFT calculations using the PW91 functional, harmonic frequencies for CO adsorbed on Ag(111) surfaces with values of 2050, 1925 and 1900 cm⁻¹ (for top, bridge and hollow sites, respectively, the top site being energetically more stable). An experimental value of 2137 cm⁻¹ for adsorbed CO on Ag(111) was obtained in HREELS measurements in UHV environment.⁶⁷ Orozco et al⁶⁸ studied the adsorption of carbon monoxide at silver electrodes in CO-saturated solutions with various pH values and reported the observation of several C-O signals in the range 1850-2050 cm⁻¹. These authors assigned to linearly bonded CO a feature at 1970-2000 cm⁻¹, which was observed for all the studied pHs. Oda et al⁶⁹ also reported the observation, for silver films deposited at platinum electrodes, of a feature around 1980 cm⁻¹ ascribed to adsorbed CO formed from dissolved CO or upon CO₂ reduction. A related feature was observed in SER spectra collected under similar conditions with roughened silver electrodes.⁶⁹ Thus, from these latter observations, it can be proposed, to explain the spectra reported in Figure 2A, that some amount of cyanate undergoes dissociation at the silver thin film electrode to form adsorbed CO. The same holds for cyanuric acid regarding the spectra in Figure 5. The difference in frequency between the UHV and spectroelectrochemical experiments is attributable to the experimental conditions, in

particular the presence of water in the interface, and, not least, to the existence of an applied potential that influences the surface charge density, that in turn can modify the extent of donation-backdonation for adsorbed CO.⁷⁰

From the latter discussion it can be concluded that adsorbed CO is formed at the silver electrode, thus implying a reactivity of both cyanate and cyanuric acid related species that was not observed in the case of gold electrodes.^{30,31} The infrared spectra collected in the cyanuric acid-containing solutions also show a higher amount of adsorbed CO at low potential when compared to that observed in cyanate-containing solutions. The detailed mechanism for the formation of adsorbed CO from adsorbed monocyanurate or cyanate species is out of the scope of this paper. However, we can connect the reactivity of both cyanuric and cyanate at silver electrodes with the observations reported for the thermal decomposition of monocyanurate silver salts to yield silver cyanate and isocyanic acid, whereas di- and trisubstituted salts give rise to the formation of silver cyanate and silver isocyanate.³⁶ Silver isocyanate was reported also to decompose into silver, carbon monoxide and molecular nitrogen at temperatures lower than those needed to decompose silver cyanate.³⁶ It can be tentatively proposed that adsorbed monocyanurate could evolve to adsorbed cyanate following the reverse process with respect to the isocyanic acid trimerization. Then, isocyanic acid could deprotonate to form adsorbed cyanate than then dissociates to yield adsorbed CO. As three isocyanic acid molecules would be formed from each monocyanurate anion, it seems reasonable that the intensity of the CO band is higher for cyanuric acid than for the cyanate containing solution. Other than the detection of adsorbed CO coming from cyanate anions and from the species formed from cyanuric acid at silver electrodes, we cannot assess whether the reaction taking place at the silver/solution interphase is the same as that proposed for the silver salts mentioned above. It is difficult to elucidate the fate of the nitrogen atoms, as molecular nitrogen is undetectable in the infrared spectra, and there is no spectroscopic evidence that could indicate the formation of other nitrogen-containing species resulting from the scission of the C-N bond.

6. Conclusions

Potential-dependent adsorption of cyanate takes place at silver electrodes in neutral solutions. This process is witnessed by the observation of an intense absorption band at ca. 2170 cm⁻¹ together with a much smaller feature at around 1320 cm⁻¹. DFT calculations indicate that these features may correspond, respectively, to the asymmetric and symmetric OCN stretching modes of N-bonded cyanate (preferentially at n-fold hollow and in a lesser extent, bridge sites). O-bonded cyanate can be discarded, as its adsorption is weaker, as reported also previously for gold surfaces. However, the small difference in adsorption energy between the adsorption on hollow

and bridge sites suggests the possible coexistence of these adsorbate geometries. The polycrystalline nature of the silver thin film electrodes used in the spectroelectrochemical experiments could give rise to a combination of adsorbates at different adsorption sites and geometries that could be at the origin of the observed widths for the asymmetric OCN stretching band in experimental spectra. Regarding the effect of adsorbate coverage, DFT calculations for various cyanate adlayers (from 1/9 to 1/2 adsorbate molecules per surface metal atom) indicate significant blueshifts (up to 75 cm⁻¹ for the asymmetric OCN stretching mode) expected when neighboring vibrations proceed in phase, as a collective vibration mode. This effect has been evidenced in the experimental spectra.

For low cyanate concentrations, adsorbed CO is detected at low potentials as indicated by the typical C-O stretching band at ca. 1980 cm⁻¹. The latter species is displaced from the electrode surface at potentials at which adsorbed cyanate prevails at the electrode surface, especially for higher cyanate concentrations in solution. Note that the formation of adsorbed CO from cyanate was not detected when a similar study was carried out at gold electrodes under these conditions.

For higher cyanate concentrations and potentials, additional bands in the ATR-SEIRA spectra can be observed between 1800 and 1300 cm⁻¹ that can be tentatively related to the formation of adsorbed cyanuric acid-related species as the result of an (electroless) trimerization reaction. As in the case of gold, the bands observed in cyanate-containing solutions are similar to those observed after dosing cyanuric acid to the sodium perchlorate solution. Taking into account the results of DFT calculations, the experimental ATR-SEIRAS results in the cyanuric acid solutions agree with the formation of adlayers of triketo-monocyanurate species adsorb perpendicular to the electrode surface. In the case of cyanate-containing solutions, a mixed layer of adsorbed N-down cyanate and adsorbed triketo-monocyanurate species is formed. In the case of gold electrodes, the bulk oxidations of cyanate and cyanuric acid are not detected voltammetrically in a potential region ranging from -0.50 to +0.60 V vs Ag/AgCl. ATR-SEIRA spectra can be obtained in the same potential range using a gold thin film deposited onto a silicon substrate. In the case of silver, the voltammetric experiments show no bulk oxidation in a potential region which is shifted to more negative values when compared to gold, namely between -0.90 and +0.20 V. Despite of these differences in the potential range explored, it can be stated that the surface processes detected for cyanate and cyanuric acids at high potentials are the same for both metals.

DFT calculations for monocyanurate adlayers with various coverages have allowed the study of the effect of vibrational coupling of neighboring adsorbates in dense adlayers on the corresponding vibrational frequencies. In this case, an additional band is observed experimentally around 1780 cm⁻¹ that is attributed to the all-in-phase collective mode that has a calculated harmonic frequency blueshifted by around 50 cm⁻¹ (at high monocyanurate coverage) with respect

to the value of the out-of-phase collective mode, that essentially coincides with that for the low coverage range.

The infrared spectra collected in the cyanuric acid-containing solutions also show a higher amount of adsorbed CO at low potential when compared to that observed in cyanate-containing solutions, thus indicating a certain unstability of cyanuric acid at the silver surfaces. The detailed mechanism for the formation of adsorbed CO from adsorbed monocyanurate or cyanate species is out of the scope of this paper. The observation of adsorbed CO mainly at low potentials suggests that the formation of oxidized nitrogen species from cyanate is unlikely. No experimental evidence was obtained that could be attributable to the presence of simple N-containing adsorbates (other than cyanate), such as NO. This suggests that the nitrogen atom could finally yield molecular nitrogen (by dimerization) or any other species that cannot compete with either cyanate or monocyanurate for the adsorption on the surface metal sites.

Supporting Information

Potential-dependent ATR-SEIRA spectra collected for a silver thin film electrode in a 0.1 M NaClO₄ solution.

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TOC graphic

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