

# Adsorption of CN at the Pt(111)/Liquid Interface by Dissociation of Acetonitrile and the Potentiality of CO Contamination: A Sum-Frequency Generation Study

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The adsorption of cyanide, CN, on the Pt(111) surface by dissociation of acetonitrile, CH<sub>3</sub>CN, has been investigated by sum-frequency generation (SFG) as surface vibrational spectroscopy and by cyclic voltammetry. The adsorption procedure involved cooling of the flame-annealed Pt crystal above a dilute aqueous solution of acetonitrile (0.1 M HClO<sub>4</sub> + 0.025 M CH<sub>3</sub>CN), followed by immersion of the sample into the electrolyte. The adsorbed species is identified as cyanide by the characteristic potential dependence of the stretching frequency, which increased from 2087 cm<sup>-1</sup> at 0.1 V to 2136 cm<sup>-1</sup> at 0.95 V, as well as by cyclic voltammetry. Comparison with the voltammogram in a 1 × 10<sup>-3</sup> M solution of CH<sub>3</sub>CN indicates that the dissociation takes place in the gas phase above the solution. A second band in our spectra with a frequency near 2155 cm<sup>-1</sup> is tentatively assigned to a Pt–cyano surface complex. We also report on experiments in which the same annealing/cooling procedure has been applied using neat liquid acetonitrile. Bands near 1860 and 2073 cm<sup>-1</sup> in SFG spectra of these samples are shown to originate from adsorbed CO, most likely produced by oxidation of CH<sub>3</sub>CN vapor at the hot Pt crystal. CN adsorption at the Pt(111)/liquid acetonitrile interface, performed by deposition of cyanide ions from solutions of tetrabutylammonium cyanide in acetonitrile, is characterized by a single band near 2110 cm<sup>-1</sup>.

## I. Introduction

One intriguing aspect of molecule–surface interactions is the relation between electronic properties of a molecule and its adsorption properties. The different electronic structures of carbon monoxide (CO) and cyanide (CN) result in different chemical interactions of these molecules with metal surfaces.<sup>1–5</sup> The most significant difference in the electronic structure of these two molecules in the gas phase is that CN has only one electron in the highest occupied molecular orbital, the 5σ orbital, which gives rise to a large electron affinity of 3.82 eV.<sup>6</sup> Due to this “5σ hole” the free CN molecule is a very reactive radical and can exist as a long-lived species only under conditions of very low molecular densities.<sup>7</sup> As a consequence, for adsorption experiments, the CN cannot be provided in the form of a laboratory gas like CO or NO. Cyanide adsorption at metal/vacuum interfaces has been achieved by dissociation of adsorbed dicyanogen, (CN)<sub>2</sub>.<sup>8,9</sup> At the metal/electrolyte interface, CN is readily adsorbed when solvated cyanide ions, (CN<sup>-</sup>)<sub>solv</sub>, are present in aqueous electrolytes.<sup>10,11</sup> It should be noted that the cyanide ion is stable only as solvated ion. The isolated CN<sup>-</sup> ion, which is isoelectronic with the stable CO and N<sub>2</sub> molecules, is an extremely reactive species, and experimental data for this ion are very scarce.<sup>12</sup>

Infrared reflection–absorption and sum-frequency generation (SFG) spectra of CN adsorbed at metal/electrolyte interfaces<sup>11,13–24</sup> revealed C–N stretching frequencies comparable to those of metal–cyano complexes.<sup>25</sup> Therefore, it has been assumed that at the metal/electrolyte interface CN adsorbs in a linear on-top geometry with its molecular axis aligned perpendicular or nearly

perpendicular to the surface. Molecularly resolved images of adsorbed CN on Pt(111) obtained with the scanning tunneling microscope are consistent with such a geometry.<sup>19,26</sup> Moreover, a common observation in vibrational studies at metal/electrolyte interfaces is that the stretching frequency of adsorbed CN is larger than that of the free CN molecule (2042.2 cm<sup>-1</sup>)<sup>7</sup> which has a bond order of 3, indicating a strengthening of the internal molecular bond upon adsorption. Cluster calculations revealed that this bond strengthening originates from charge depletion of the antibonding 4σ CN orbital when the molecule adsorbs in a linear geometry at on-top sites, that the linear on-top geometry is the only geometry compatible with a C–N stretching frequency above that of the isolated molecule, and that bonding through the carbon atom yields the largest adsorption energy. Moreover, with 0.3e charge transferred from the Pt surface atoms to the CN group, adsorbed CN does not carry a full (negative) electronic charge.<sup>5</sup>

A major puzzle that has not been resolved so far is the observation of a different adsorption geometry of CN at metal/vacuum interfaces. A decrease of the stretching frequency to values between 1770 and 1930 cm<sup>-1</sup>, indicative of a rehybridization of the internal C–N bond to a bond order of about 2.5, was observed after CN formation on Pd(111) and Pd(100) surfaces under vacuum conditions by dissociation of dicyanogen.<sup>9,27,28</sup> Furthermore, the low intensity of the C–N stretching vibration (in comparison with that of the CN–metal stretching vibration) was interpreted to be indicative of a flat-lying geometry of the adsorbed CN. This proposed adsorption geometry was confirmed by near-edge X-ray absorption fine structure (NEXAFS) experiments on the Pd(111) surface.<sup>29</sup> This situation is in marked contrast to CO adsorption at the Pt(111) surface: the internal C–O stretching frequencies, signatures of the CO–metal interaction and the local adsorption geometry,<sup>4,5</sup> are comparable at Pt/electrolyte and Pt/vacuum interfaces<sup>30–35</sup>

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(with the exception that CO adsorption at 3-fold hollow sites is in general not observed for the clean Pt(111)/vacuum interface).

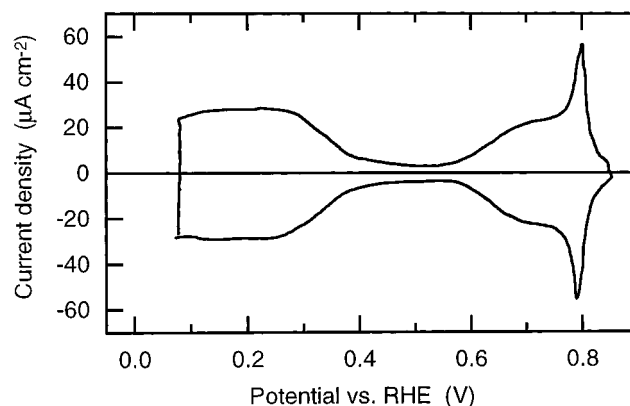
In this paper we report CN adsorption on Pt(111) by a procedure that does not require dissociation of dicyanogen in ultrahigh vacuum and does not make use of hydrated cyanide ions in aqueous solutions. CN was adsorbed by dissociation of acetonitrile ( $\text{CH}_3\text{CN}$ ) molecules at a hot Pt(111) surface that was cooled above an aqueous solution of 0.025 M  $\text{CH}_3\text{CN}$  + 0.1 M  $\text{HClO}_4$ . We also point out the risk of contaminations by adsorbed CO, which yields much larger band intensities. Samples prepared by cooling the annealed Pt sample above neat acetonitrile exhibited SFG spectra with strong bands near 1860 and 2073  $\text{cm}^{-1}$ , which we have previously assigned to CN adsorbed at hollow and on-top sites, respectively.<sup>5</sup> However, additional experiments discussed in this paper provide evidence that this assignment is incorrect and that the bands originate from adsorbed CO that most likely was produced by oxidation of acetonitrile molecules.

## II. Experimental Section

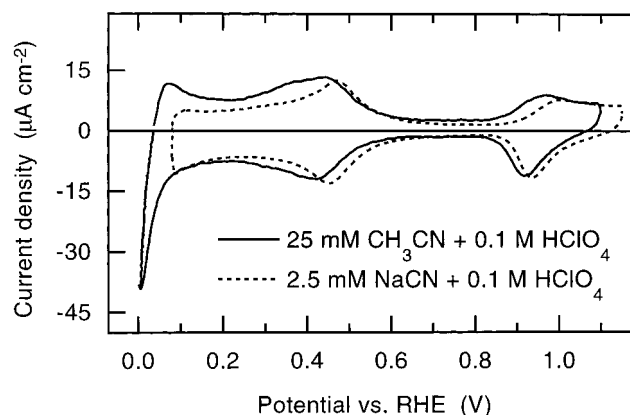
We used cylindrical, (111)-oriented Pt single crystals of 10 mm diameter and about 3 mm thickness. The mechanically polished surfaces were oriented to within  $0.5^\circ$  from the nominal surface orientation and were cleaned by prolonged heating in an oxygen atmosphere at 990  $^\circ\text{C}$  to deplete the bulk of carbon and sulfur contamination. The final cleaning procedure consisted of standard flame annealing to yellow heat in a flame from a propane/butane gas mixture, followed by immediate transfer into an electrochemical glass cell. In the cell, the annealed crystals were allowed to cool for some minutes, with the Pt(111) surface 1–2 cm above the surface of the liquids, which were either aqueous electrolytes or acetonitrile. The liquids as well as the cell volume above them were purged with Ar gas (Messer Griesheim, purity 99.999%). Aqueous electrolytes were prepared from purified water supplied by a Milli-Q Plus system (Millipore, TOC <10 ppb,  $\rho > 18 \text{ M}\Omega\cdot\text{cm}$ ), and  $\text{HClO}_4$  (Merck, Suprapur). Acetonitrile (Merck, pro analysi) was used as received. NaCN (Merck, pro analysi) and tetrabutylammonium cyanide (TBACN, Fluka, purum) were used to adsorb CN from aqueous solutions and nonaqueous solutions in acetonitrile, respectively. For solutions of acetonitrile in aqueous electrolytes, we can specify only the initial concentrations because of the high volatility of acetonitrile.

Details of the cell used for both cyclic voltammetry and SFG can be found elsewhere.<sup>36</sup> SFG experiments were conducted in a thin-layer configuration with an effective thickness of the liquid layer of about 1–2  $\mu\text{m}$  in order to minimize IR absorption in the liquid. As reference electrode we used a reversible hydrogen electrode (RHE), and the potentials quoted in this work refer to this electrode.

After immersion of the flame-annealed crystal into a 0.1 M aqueous solution of  $\text{HClO}_4$ , the voltammogram characteristic of a clean Pt(111) electrode was obtained (Figure 1). The immersion potential after flame annealing was chosen to lie in the double-layer potential range of the clean Pt(111) electrode in 0.1 M  $\text{HClO}_4$ , between 0.45 and 0.55 V. After CN adsorption and voltammetric characterization of the sample, the electric circuit had to be opened to move the cell into the SFG spectrometer. To establish stable electrochemical conditions in the absence of potentiostatic control, hydrogen gas was evolved for 10 s before disconnection, and the bias was reconnected at a potential of 0.7 V, which is within the double-layer region of the CN-covered Pt(111) electrode (Figure 2). Experiments with neat acetonitrile and with solutions of TBACN in acetonitrile



**Figure 1.** Cyclic voltammogram of Pt(111) in an aqueous solution of 0.1 M  $\text{HClO}_4$ . The scan rate was 50 mV/s.

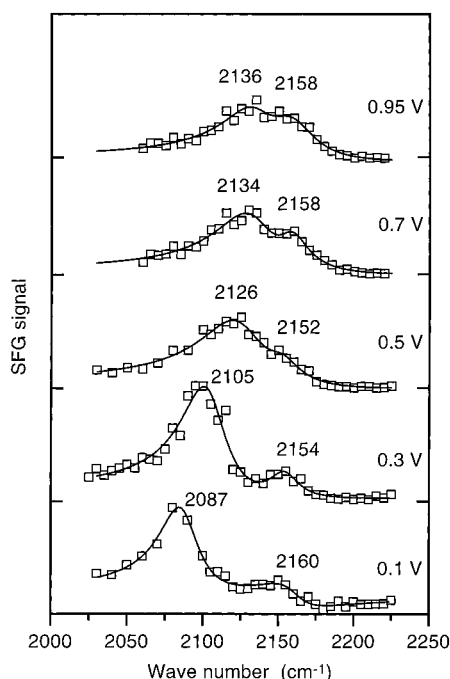


**Figure 2.** Solid line: cyclic voltammogram of Pt(111) in an aqueous solution of 0.025 M  $\text{CH}_3\text{CN}$  + 0.1 M  $\text{HClO}_4$  after cooling the flame-annealed crystal for 6 min above the solution. Dotted line: cyclic voltammogram of Pt(111) in an aqueous solution of 2.5 mM NaCN + 0.1 M  $\text{HClO}_4$ . The scan rates were 50 mV/s.

were performed on uncharged Pt surfaces without applied potential. In some experiments we adsorbed CO by bubbling CO gas (Messer Griesheim, purity 99.997%) for several minutes into the liquid until the solution was saturated.

Vibrational spectra of adsorbed molecules were obtained by infrared-visible SFG. The vibrations were excited by 19 ps mid-infrared pulses from a tunable optical parametric infrared converter.<sup>37</sup> The repetition rate of the laser pulses was 10 Hz. For SFG, these infrared pulses were superimposed at the interface to 22 ps laser pulses of 532 nm wavelength in a near-collinear geometry. Both beams were p-polarized, and the angle of incidence was approximately  $60^\circ$ . Only the p-polarized component of the sum-frequency signal was detected. Pulse energies were typically 100  $\mu\text{J}$  for the infrared beam and 400  $\mu\text{J}$  for the green laser beam, and the fluences of both beams were below 5  $\text{mJ cm}^{-2}$ . To account for the wavelength dependence of the pulse energy and the spatial beam characteristics as well as for laser power drifts and pulse energy fluctuations, the SFG signal from the Pt sample was normalized to the SFG signal simultaneously generated with the sample signal in the bulk of a polycrystalline ZnS reference sample situated in air. The signals were detected with a photomultiplier after spectral discrimination with optical filters and monochromators. The wavelength increments were 5 or 10  $\text{cm}^{-1}$ . Spectra were collected by averaging the signals of 200 or 300 laser pulses for each frequency.

The SFG spectra were analyzed in terms of vibrational resonances due to adsorbed molecules, and a frequency-



**Figure 3.** SFG spectra of a flame-annealed Pt(111) crystal that was cooled above an aqueous solution of 0.1 M HClO<sub>4</sub> + 0.025 M CH<sub>3</sub>CN, immersed, and cycled between 0.01 and 1.1 V to yield the voltammogram shown in Figure 2. The solid lines are fits to the data using eq 1.

independent contribution.<sup>38</sup> As a model for the frequency dependence of the sum-frequency susceptibility  $\chi^{(2)}$ , we used

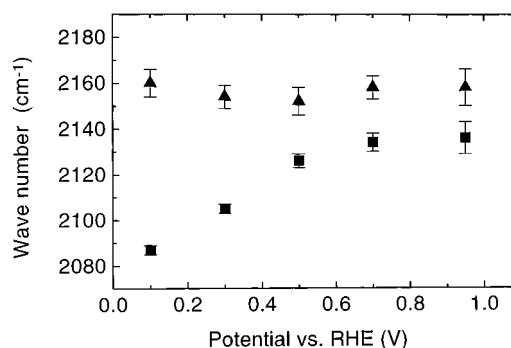
$$\chi^{(2)} = A_0 + \sum_{k=1}^n \frac{A_k e^{i\phi_k}}{\omega_{\text{ir}} - \omega_k + i\gamma_k/2} = \chi_{\text{NR}}^{(2)} + \chi_{\text{R}}^{(2)}(\omega_{\text{ir}}) \quad (1)$$

$\chi_{\text{NR}}^{(2)}$  originates from electronic excitations of the interface that are resonant with the sum frequency. The frequency dependence of  $\chi_{\text{NR}}^{(2)}$  can be neglected on the scale of the molecular vibrations discussed below. The amplitudes  $A_0$  and  $A_k$ , the vibrational frequencies  $\omega_k$ , the line widths  $\gamma_k$  (fwhm), and the phases  $\phi_k$  are parameters to fit the calculated SFG intensity  $I_{\text{SFG}} \propto |\chi^{(2)}|^2$  to the measured spectra.

### III. Results and Discussion

**A. CN/Pt(111) in Aqueous Electrolytes.** In Figure 3 we present SFG spectra obtained from a flame-annealed Pt(111) sample that was cooled for about 6 min above an aqueous solution of 0.1 M HClO<sub>4</sub> + 0.025 M CH<sub>3</sub>CN, immersed into the electrolyte, and cycled between 0.01 and 1.1 V to yield the voltammogram shown as a solid line in Figure 2. The SFG spectra of this surface exhibit two bands with quite different potential dependencies. As discussed below, we assign these two bands to C–N stretching vibrations of two different species adsorbed on the Pt surface. The frequency of the band that dominates at lower potentials has a strong, nonlinear potential dependence and increases from 2087 to 2136 cm<sup>−1</sup>, while the frequency of the second band near 2155 cm<sup>−1</sup> shows no potential dependence within experimental error. The variation of the frequencies with the potential is displayed in Figure 4. The potential dependence of the SFG intensities will be discussed further below.

Our assignment of the two bands in Figure 3 is based on their frequencies and the large potential range of adsorption. CO as a possible adsorption product can be ruled out because



**Figure 4.** Variation of the C–N stretching frequencies with the potential, as obtained from the fits in Figure 3.

(1) the frequencies of adsorbed CO on Pt(111) are consistently below 2096 cm<sup>−1</sup> in nonaqueous electrolytes and below 2076 cm<sup>−1</sup> in 0.1 M aqueous solutions of HClO<sub>4</sub><sup>31</sup> and (2) adsorbed CO is electro-oxidized to CO<sub>2</sub> and desorbs at about 0.78 V in a CO-free, 0.1 M aqueous solution of HClO<sub>4</sub>.<sup>39</sup> In contrast, the bands of the adsorbed species are present in our SFG spectra at potentials as high as 1 V.

The frequencies of the two bands in Figure 3, as well as their potential dependencies,<sup>40</sup> are in good agreement with SFG spectra previously reported for cyanide adsorption on Pt(111) and Pt(110) surfaces by deposition of solvated cyanide ions from aqueous electrolytes.<sup>21</sup> Consistent with the conclusions in that paper and with results of cluster calculations,<sup>5</sup> we assign the band with the lower frequency to CN adsorbed via the C atom in an on-top geometry on terraces of the Pt surface. The frequencies of this band are in good agreement with the results by Huerta et al., who studied CN on Pt(111) in a cyanide-free, 0.1 M HClO<sub>4</sub> electrolyte by infrared spectroscopy after CN adsorption from an aqueous solution of KCN.<sup>22</sup>

The high frequency of the second band, 2155 cm<sup>−1</sup>, and the insensitivity of its frequency to a variation of the potential, which is unusual for small molecules chemisorbed at metal/electrolyte interfaces, point to a cyanide species that is substantially different from CN adsorbed at the regular Pt surface atoms of the microscopically flat Pt(111) surface. There is agreement<sup>42</sup> in the literature that this band is related to a more disordered surface<sup>18–21</sup> and it has been tentatively assigned to the formation of a [Pt(CN)<sub>2</sub>]<sup>2−</sup> complex or a related Pt–cyano complex on the Pt surface, promoted by surface disorder.<sup>18,21</sup> We note that this band, which is absent for a well-ordered Pt(111) surface,<sup>18,19,21–24</sup> was not consistently observed in our present experiments, presumably because of varying conditions of surface disorder. We also note that the features of the voltammogram in Figure 2 appeared to be insensitive to the presence of this species.

Our assignment of the spectra in Figure 3 to adsorbed CN is consistent with the voltammogram of the surface recorded before collecting the SFG spectra. This voltammogram is shown as the solid line in Figure 2 and closely resembles the one reported by Huerta et al. for a CN-covered Pt(111) electrode surface in a cyanide-free, 0.1 M HClO<sub>4</sub> electrolyte.<sup>22</sup> A voltammogram identical to the solid line in Figure 2 was also obtained with a 0.05 M solution of CH<sub>3</sub>CN. The voltammograms were reversible and reproducible after cycling the potential several times between 0.01 and 1.1 V. For comparison, we also show, as the dotted line in Figure 2, the voltammogram that we obtained after cyanide adsorption on Pt(111) in an aqueous electrolyte of 2.5 × 10<sup>−3</sup> M NaCN + 0.1 M HClO<sub>4</sub>. In this experiment, we cooled the annealed Pt(111) surface in an Ar atmosphere in a separate cell with a 0.1 M HClO<sub>4</sub> electrolyte that contained

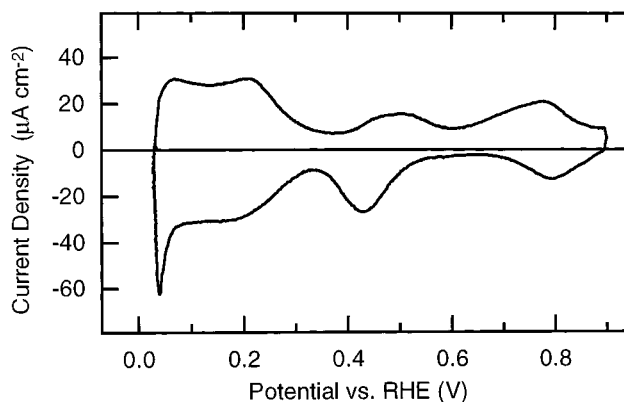


no acetonitrile or cyanide ions. After immersion into the cyanide-free electrolyte, the clean Pt sample, protected with a drop of electrolyte on the surface, was transferred at room temperature into the cell containing the electrolyte with cyanide. With this procedure we ensured that cyanide adsorption occurred only through deposition of solvated  $\text{CN}^-$  ions from the electrolyte and not by dissociation of HCN molecules in the gas phase that might have been formed from the acidic solution. The voltammogram recorded in the  $2.5 \times 10^{-3}$  M NaCN + 0.1 M  $\text{HClO}_4$  electrolyte agrees with that reported by Kim et al.<sup>26</sup> for a solution of  $0.1 \times 10^{-3}$  M NaCN + 0.1 M  $\text{HClO}_4$ .

The similarity of the two voltammograms in Figure 2 provides additional proof that our sample preparation described above yielded a CN-covered Pt surface. Minor differences between the two voltammograms, such as the less pronounced adsorption/desorption features around 0.45 V for the sample prepared by cooling above the  $\text{CH}_3\text{CN}$ -containing solution, and the slightly different potentials of this feature and of the anodic features above 0.9 V in comparison with the voltammogram in the  $2.5 \times 10^{-3}$  M NaCN + 0.1 M  $\text{HClO}_4$  electrolyte may be attributed to the absence of  $\text{CN}^-$  and  $\text{Na}^+$  ions and/or the presence of  $\text{CH}_3\text{CN}$  molecules.

As pointed out by Kim et al.,<sup>26</sup> and as can be seen by comparing the voltammogram of the bare Pt(111) surface in Figure 1 to those of the CN-covered surfaces in Figure 2, hydrogen adsorption between 0 and 0.4 V is only partially suppressed by the adsorption of cyanide, contrary to the case of CO adsorption.<sup>39</sup> Furthermore, these authors observed a structural change of the CN adlayer from a  $2\sqrt{3} \times 2\sqrt{3}R30^\circ$  structure with a coverage of 0.583 for potentials above 0.5 V to a  $\sqrt{7} \times \sqrt{7}R19^\circ$  structure with a coverage of 0.57 between 0.2 and 0.4 V,<sup>26</sup> which implies a small coverage variation of about 2%. On a first view, the pronounced decrease of SFG signal between 0.3 and 0.5 V observed for the band with the lower frequency in Figure 3 appears to be inconsistent with such a small change of coverage. However, the analysis of our SFG spectra using the model function in eq 1 showed that in this potential range the SFG amplitude of the lower-frequency band changes only by 10%, which is within the error limits of our analysis. The marked decrease of intensity between 0.3 and 0.5 V originates from a decrease of the vibrationally nonresonant electronic contribution, which enhances the intensity of the vibrational bands by interference according to eq 1. A decrease of the nonresonant contribution with increasing values of the potential was also observed for the bare Pt(111) electrode surface in 0.1 M  $\text{HClO}_4$ .<sup>41</sup>

Applying the same cooling procedure above an aqueous solution of  $1 \times 10^{-3}$  M  $\text{CH}_3\text{CN}$  + 0.1 M  $\text{HClO}_4$ , we obtained the voltammogram in Figure 5. No discernible signals of C–N stretching vibrations between 2000 and 2200  $\text{cm}^{-1}$  could be observed in the SFG spectra of these samples. The voltammogram in Figure 5 is much different from those of the CN-covered electrodes in Figure 2 but agrees with the voltammogram reported by Morin and Conway<sup>43</sup> for acetonitrile adsorption on Pt(111) in a solution of  $0.8 \times 10^{-4}$  M  $\text{CH}_3\text{CN}$  + 0.1 M  $\text{HClO}_4$ . The absence of a C–N stretching band in the 2000–2200  $\text{cm}^{-1}$  range is consistent with nondissociative adsorption of acetonitrile at the Pt(111)/aqueous electrolyte interface. Using infrared spectroscopy, Morin et al.<sup>44</sup> investigated the chemisorption of acetonitrile on Pt(111) in a solution of  $7 \times 10^{-3}$  M  $\text{CH}_3\text{CN}$  + 0.1 M  $\text{HClO}_4$ . They reported a C–N stretching band at 1630  $\text{cm}^{-1}$  and assigned it to a reduced form of chemisorbed acetonitrile with a rehybridized nitrile group of bond order 2. The absence of absorption bands between 2000 and 2200  $\text{cm}^{-1}$

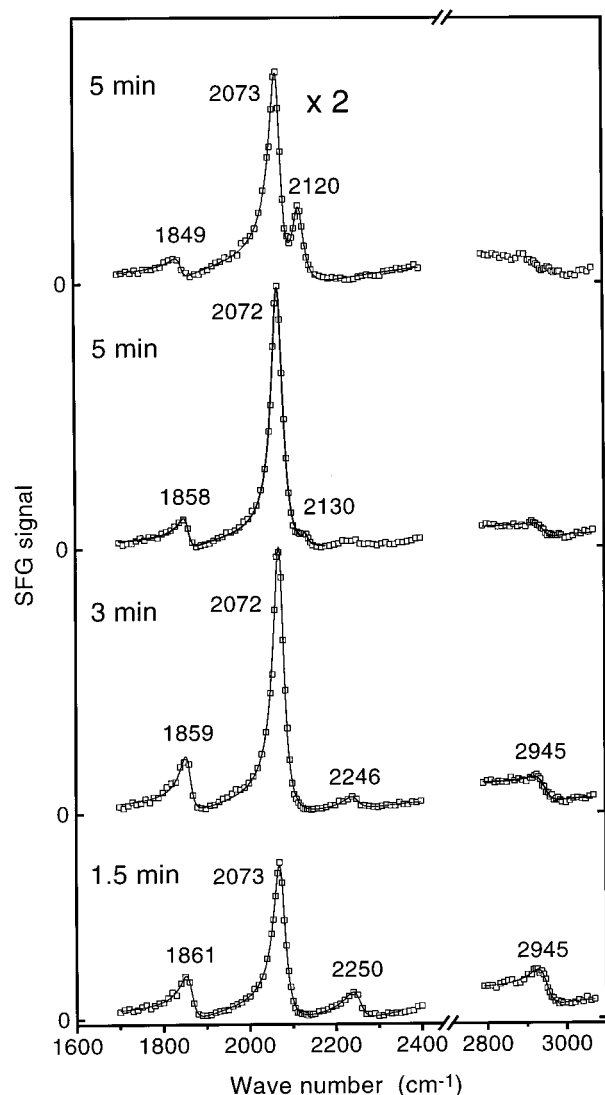


**Figure 5.** Cyclic voltammogram of Pt(111) in an aqueous solution of  $1 \times 10^{-3}$  M  $\text{CH}_3\text{CN}$  + 0.1 M  $\text{HClO}_4$  after cooling the flame-annealed crystal for 6 min above the solution. The scan rate was 50 mV/s.

in their infrared spectra rules out detectable amounts of adsorbed cyanide on their Pt(111) electrodes.

Given the fact that these studies did not indicate cyanide adsorption on the Pt(111) surface for a relatively wide range of acetonitrile concentrations ( $8 \times 10^{-5}$  M to  $7 \times 10^{-3}$  M), we consider it unlikely that in our experiments with a  $25 \times 10^{-3}$  M concentration of  $\text{CH}_3\text{CN}$  the observed cyanide adsorption proceeded via dissociation of acetonitrile molecules in the solution. Taking into account that the partial pressure of  $\text{CH}_3\text{CN}$  vapor above the  $25 \times 10^{-3}$  M solution is much larger than above the  $1 \times 10^{-3}$  M solution, we conclude that CN was adsorbed in our experiments through thermally activated dissociation of  $\text{CH}_3\text{CN}$  molecules during the cooling period when the annealed Pt crystal was exposed to the vapor of the solution. Unfortunately, from our experimental data we cannot identify the relevant dissociation reaction or intermediates of CN adsorption. As possible dissociation products of acetonitrile we consider dicyanogen ( $(\text{CN})_2$ ), the CN radical itself, and hydrogen cyanide (HCN).  $(\text{CN})_2$  has been shown to adsorb dissociatively as CN on Pd(111) at 300 K.<sup>29</sup> It was reported that HCN adsorbs dissociatively as H and CN on Pt(111).<sup>45,46</sup> Above 200 K, partial recombination of H and CN to adsorb aminomethyldyne was observed, however.<sup>46</sup> Noteworthy, the CN frequencies and band intensities, as observed in our present experiments at the Pt(111)/electrolyte interface, are characteristic of a linear on-top adsorption configuration of CN with a bond order of 3, while at the Pt/vacuum<sup>46</sup> and at the Pd/vacuum<sup>29</sup> interface the CN bond axis was found to be parallel to the surface, and the bond order was about 2.5 in the case of Pd.<sup>29</sup>

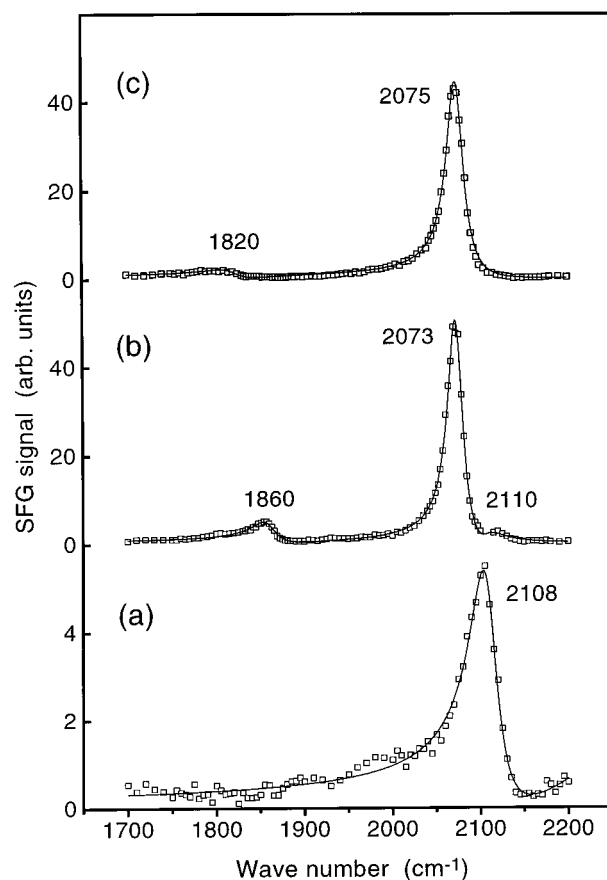
**B. Results for Neat Acetonitrile: Adsorption of CO Produced by Oxidation of Acetonitrile.** In Figure 6 we present SFG spectra obtained after cooling the annealed Pt(111) sample above neat liquid acetonitrile and immersion into the liquid without applied potential. The time elapsed between transfer of the annealed crystal with orange heat into the cell and immersion into the liquid was varied between 1.5 and 5 min. The spectra exhibit a very strong band near 2073  $\text{cm}^{-1}$  and a weaker band in the range between 1850 and 1860  $\text{cm}^{-1}$ . The intensity of the 1860  $\text{cm}^{-1}$  band tends to decrease in Figure 6 with increasing cooling time relative to the intensity of the 2073  $\text{cm}^{-1}$  band, but this tendency was not consistently reproduced in other experiments in which the crystal was allowed to cool for up to 9 min. The intensity of the 2073  $\text{cm}^{-1}$  band in Figure 6 was comparable to that of terminally adsorbed CO in SFG spectra of Pt(111)–CO/electrolyte interfaces.<sup>36</sup> In some experiments, a band with a frequency between 2110 and 2130  $\text{cm}^{-1}$  was observed, either as a weak shoulder of the 2072  $\text{cm}^{-1}$  band



**Figure 6.** SFG spectra of a flame-annealed Pt(111) crystal that was cooled above and subsequently immersed into neat liquid acetonitrile. The cooling time is indicated for each spectrum. The solid lines are fits to the data using eq 1. The topmost spectrum is magnified by a factor of 2.

or as a well-resolved peak at  $2120\text{ cm}^{-1}$ , as seen in the two topmost spectra in Figure 6. In addition, some spectra showed bands near  $2248$  and  $2945\text{ cm}^{-1}$ . These frequencies compare well with the stretching vibration of the nitrile group ( $2254\text{ cm}^{-1}$ ) and the symmetric stretching vibration of the methyl group ( $2944\text{ cm}^{-1}$ ), respectively, of bulk liquid acetonitrile.<sup>47</sup> We therefore assign these bands to acetonitrile molecules that could have either coadsorbed at the Pt/liquid acetonitrile interface<sup>48</sup> or adsorbed at the liquid acetonitrile/ $\text{CaF}_2$  interface.<sup>49</sup>

Now we discuss the bands near  $1860$  and  $2073\text{ cm}^{-1}$  in Figure 6. These bands correspond to species adsorbed at the Pt(111) surface, and they must originate from reaction products of acetonitrile. We have shown in section IIIA that cooling of the annealed Pt crystal above an aqueous solution of acetonitrile resulted in CN adsorption. Replacing the aqueous solution of acetonitrile by neat acetonitrile with a much larger vapor pressure, we expected the CN adsorption to be even more efficient. For this reason we have previously identified the bands near  $1860$  and  $2073\text{ cm}^{-1}$  in Figure 6 with CN adsorbed at two different adsorption sites.<sup>5</sup> We have assigned these bands to CN adsorbed through the carbon atom at hollow and on-top sites, respectively, of the Pt(111) surface; as for these adsorption



**Figure 7.** SFG spectra of Pt(111)/acetonitrile interfaces. (a) Spectrum after adsorption of CN on Pt(111) from a solution of  $0.012\text{ M}$  tetrabutylammonium cyanide in acetonitrile. (b) Spectrum after cooling an annealed Pt(111) surface for  $8\text{ min}$  above liquid acetonitrile and immersion. (c) Spectrum after CO adsorption on Pt(111) in acetonitrile. In all three experiments no potential was applied to the samples. Notice the 10-fold magnification of spectrum (a). The solid lines are fits to the data using eq 1.

geometries, a good agreement was obtained between the measured frequencies and the frequencies calculated for CN adsorption on a  $\text{Pt}_{25}$  cluster.<sup>5</sup> The appearance of an additional band in the  $2110\text{--}2130\text{ cm}^{-1}$  range in some of the spectra with an intensity that strongly varied from experiment to experiment (see Figure 6) was taken as additional indication for cyanide adsorption, for this band was identified with a cyanide species related to a more disordered Pt surface, in analogy to the  $2155\text{ cm}^{-1}$  band in Figure 3 observed at the Pt(111)/aqueous electrolyte interface.<sup>50</sup>

However, additional spectroscopic data presented and discussed below led us to revise our previous assignment of the bands near  $1860$  and  $2073\text{ cm}^{-1}$  in favor of an interpretation in terms of adsorbed CO and led us to the conclusion that our adsorption procedure using neat acetonitrile allows for a large CO contamination of the surface. Our revised assignment of the bands is based on a comparison of spectra from samples prepared by the cooling procedure described above with spectra from CN- and CO-covered Pt(111) surfaces in acetonitrile. Importantly, this assignment accounts in a consistent way for the very different intensities of the various bands in Figures 3 and 6.

Spectrum a in Figure 7 was obtained after cooling a flame-annealed sample for  $6\text{ min}$  in an argon atmosphere and transferring the clean sample at a temperature well below  $100^\circ\text{C}$  without applied potential into a solution of  $0.012\text{ M}$  tetrabutylammonium cyanide (TBACN) in acetonitrile. In this

way, dissociative reactions of  $\text{CH}_3\text{CN}$  molecules in the vapor phase at the hot Pt surface were avoided, and it was ensured that CN was adsorbed exclusively by deposition of solvated cyanide ions. The spectrum exhibits a single band at  $2108\text{ cm}^{-1}$  due to CN adsorbed in a linear geometry at on-top sites of the Pt(111) surface. In other experiments with  $0.025\text{ M}$  solutions of TBACN in acetonitrile, the band was observed at somewhat higher frequencies between  $2114$  and  $2119\text{ cm}^{-1}$ . In any case, the frequencies of CN adsorbed by deposition from TBACN/acetonitrile solutions are consistent with the CN frequency in Figure 3 (at a potential of about  $0.3\text{ V}$ ) and with CN frequencies (at a corresponding potential) reported in previous studies of cyanide adsorption at Pt(111) in aqueous electrolytes.<sup>18,19,21–24</sup> No bands with lower frequencies indicative of CN adsorption at bridge or hollow sites<sup>5</sup> are observed in spectrum a of Figure 7. Moreover, the SFG signal of the CN band in spectrum a was comparable to that of the lower-frequency band at  $0.3\text{ V}$  in Figure 3.

Spectrum b in Figure 7 was obtained with the same procedure as the spectra in Figure 6. Comparing spectrum b with spectrum a, one should notice the order-of-magnitude difference in the SFG signal and a difference in frequency of  $35\text{ cm}^{-1}$  between the  $2073\text{ cm}^{-1}$  band in (b) and the  $2108\text{ cm}^{-1}$  CN band in (a), while the weak shoulder at  $2110\text{ cm}^{-1}$  in (b) matches the CN frequency in (a).

Spectrum c in Figure 7 represents a CO-covered Pt(111) surface in acetonitrile. This spectrum was obtained after exposing a CN-free Pt(111) surface in acetonitrile without applied potential to CO gas, which was bubbled into the liquid until saturation. In accordance with a previous adsorption study of CO on Pt(111) in acetonitrile by Chang et al.,<sup>31</sup> the band at  $2075\text{ cm}^{-1}$  can be assigned to CO adsorbed at on-top sites and the band at  $1820\text{ cm}^{-1}$  to CO adsorbed at 3-fold hollow sites. For an electrolyte of  $0.15\text{ M}$  tetrabutylammonium phosphate in acetonitrile, these authors reported CO frequencies of  $1810$  and  $2075\text{ cm}^{-1}$  at about  $0\text{ V}$  potential vs the saturated calomel electrode (SCE).<sup>31</sup> The weak SFG intensity of CO at hollow sites in spectrum c is consistent with previous SFG studies of CO adsorption on Pt(111)<sup>36,51</sup> and has been attributed to an interference effect.<sup>51</sup>

The striking similarity of the band at  $2073\text{ cm}^{-1}$  in spectrum b with the CO band at  $2075\text{ cm}^{-1}$  in spectrum c, with respect to both frequency and intensity, and the dramatic differences between spectrum b and spectrum a can be explained in a consistent way only if the bands near  $2073\text{ cm}^{-1}$  in spectrum c and in Figure 6 are assigned to CO molecules adsorbed at on-top sites. Consequently, the bands near  $1860\text{ cm}^{-1}$  in spectrum b and in Figure 6 should also be assigned to CO molecules, adsorbed at bridge or near-bridge sites,<sup>32</sup> and not to CN at hollow sites as has been proposed previously.<sup>5</sup>

Now that we have established that the bands near  $1860$  and  $2073\text{ cm}^{-1}$  in Figure 6 originate from adsorbed CO and not from adsorbed CN, we briefly discuss how the contaminating CO could have been produced. In our experiments the liquids were constantly purged with argon gas. We therefore rule out that CO was adsorbed after immersing the Pt sample into acetonitrile. As a likely scenario, CO was formed by oxidation of acetonitrile when the hot Pt crystal ( $T > 800\text{ }^\circ\text{C}$ ) approached the aperture of the cell and heated an air/acetonitrile/argon gas mixture produced by evaporated acetonitrile, which escaped from the Ar-purged cell. With some CO gas accumulated in the cell, CO adsorption at the Pt surface could have taken place when the temperature of the Pt surface fell below the desorption temperature of CO.<sup>33,52</sup> The much smaller  $\text{CH}_3\text{CN}$  pressure of

the vapor above dilute aqueous solutions of acetonitrile is the most likely reason CO was not produced in measurable concentrations in our experiments with  $0.025\text{ M}$  solutions of  $\text{CH}_3\text{CN}$  in  $0.1\text{ M HClO}_4$  (section IIIA).

Finally, we discuss the adsorbed species with a frequency near  $2120\text{ cm}^{-1}$  in the two topmost spectra of Figure 6 and in spectrum b of Figure 7. Comparison of this spectral feature with spectrum a in Figure 7 strongly suggests that it should be assigned to CN molecules coadsorbed with CO at the Pt(111) surface. The strong intensity variation of this band in our experiments from zero to an appreciable level, as shown in Figure 6, does therefore not reflect different structural conditions of the Pt surface but different CN coverages in the coadsorption of CO and CN, resulting from varying conditions for CO and CN formation from acetonitrile vapor.

#### IV. Conclusion

We have shown that CN can be adsorbed on Pt(111) by dissociation of  $\text{CH}_3\text{CN}$  molecules when the annealed and hot Pt surface is cooled above an aqueous solution of perchloric acid containing  $0.025\text{ M CH}_3\text{CN}$ . After immersion into the electrolyte, the vibrational signature of the adsorbed CN species is very similar to that of a CN adlayer prepared by deposition of hydrated cyanide ions from aqueous electrolytes. Application of the same annealing/cooling procedure to neat acetonitrile yielded spectra with strong bands near  $1860$  and  $2073\text{ cm}^{-1}$ . These bands were shown to originate from adsorbed CO that was most likely produced by oxidation of acetonitrile in the vapor phase. We also reported spectra that demonstrate the coadsorption of CN and CO on Pt(111).

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