Raman Spectrum of Carbon Monoxide on a Platinum Electrode Surface

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Summary The Raman spectrum of CO adsorbed on a platinized platinum electrode surface exhibited a weak line at 2096 cm^{-1} and a broader feature centred at *ca.* 2081 cm^{-1}; these features have been interpreted in terms of terminal surface $-C{\equiv}O$ groupings.

While the adsorption of carbon monoxide on platinum surfaces has been the subject of intensive and diverse spectroscopic research, no Raman data have yet been reported for this system either for gas–solid ('dry') surfaces or electrochemical ('wet') surfaces. In an electrochemical context, the adsorption of carbon monoxide on platinum in acidic media has been thoroughly investigated using voltammetric techniques.[1] The recent successful application of high surface-area platinized platinum electrode surfaces in Raman spectroscopic studies[2] has led to the present attempt to detect lines arising from carbon monoxide on these surfaces.

The spectra reported were recorded on a modified Coderg T800 spectrometer coupled to a Spectra Physics 170 argon ion laser. An EMI9558 phototube was used as detector. A Hamner N780A photon ratemeter and a Hi-Tek PA-1 signal averager were used in conjunction with the rapid repeat-scan facility of the spectrometer to generate, at each potential, spectra which are signal-averaged over either 64 or 128 scans. A Hi-Tek DT 2101 potentiostat was used to control the potential of the working electrode. A saturated calomel electrode (SCE) was employed as reference and all voltages are quoted relative to that standard. Comparable spectra obtained using a $Hg-Hg_2SO_4$ reference confirmed that chloride diffusion was not significantly suppressing[1] carbon monoxide adsorption.

Both potentiostatic and galvanostatic platinization from 0·05 M chloroplatinic acid solution were employed in developing surfaces suitable for Raman spectroscopic investigation. To assist in the formation of grey rather than black deposits,† the use of the usual lead acetate additive[3] was omitted. The galvanostatic method was qualitatively similar to reported methods[3] except that much longer periods of current reversal (15—30 min) and longer periods of platinization were used. In general, however, potentiostatic methods were found to be more convenient. In this approach, the working electrode, after cleaning in *aqua regia* and triply distilled water, was held at -130 mV for *ca.* 30 min. The typical cell current flowing was *ca.* 6 mA cm^{-2}. The resultant surface was grey in colour. The shade of the deposit could be conveniently varied by adjusting the working electrode potential in the range -100 to -150 mV and by varying the period of deposition. After cleaning and H_2 to O_2 cycling pretreatment in acid solution, the grey electrode surface produced hydrogen

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† Black surfaces are undesirable as they absorb the radiation causing local heating and also reduce the efficiency of scattering from the Raman system.

adsorption–desorption voltammetric waves similar to those described for flat surfaces,[4] but having a larger amplitude.

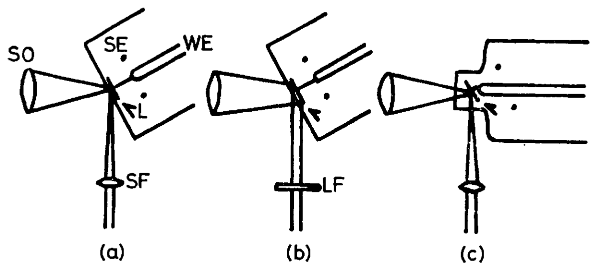

Figure 1. Modes of electrode surface illumination: SO, spectrometer optics; WE, working electrode; SE, subsidiary electrode; L, Luggin capillary; SF, 'spot' focusing lens; and LF, 'line' focusing cylindrical lens.

Three types of electrode illumination were employed (Figure 1). Both conventional 'spot' focusing and also 'line' focusing of the laser (using a cylindrical lens) were employed in different experiments. In addition, the arrangement in Figure 1c was tested. In this case light reflection losses at the glass surfaces are minimized. The 'line' illumination in Figure 1b appeared to produce the best results for the CO–Pt system.

According to previous voltammetric studies[1] carbon monoxide adsorbs as a monolayer on Pt between +0·2 and +0·8 V. At +0·8 V the platinum surface oxidizes. In the present experiments the platinized surface was cycled in the 1 M H_2SO_4 electrolyte between H_2 and oxygen evolution for 10 min before being allowed to stand at H_2 evolution for 5 min at the completion of the terminating cycle. The potential was then adjusted to +0·4 V where the signal-averaged (× 64) background spectrum was recorded. Without disturbing the cell, the solution was then saturated with CO over a period of 90 min. A signal-averaged spectrum at the unchanged potential (+0·4 V) was then recorded (Figure 2) revealing a weak line at 2096 cm^{-1} and a broader feature at *ca.* 2081 cm^{-1}. These results compare with i.r. frequencies reported[5] for CO on dry Pt surfaces which range from 2040 to 2075 cm^{-1}, and which are very sensitive to the presence of other adsorbates. To confirm that the observed Raman lines behave in the fashion predicted[1] for adsorbed CO, the potential was adjusted to +0·9 V when, as anticipated,[1] the two lines were no longer detectable. Attempts to record spectra of the solution of 1 M H_2SO_4 saturated with CO by itself at similar experimental sensitivities to those described above reveal no lines in the region, other than the extremely broad 'association' band[6] of liquid water at *ca.* 2125 cm^{-1}. The sharp increase in background at *ca.* 2150 cm^{-1} represents the leading edge of a band originating in the glass flat of the spectroscopic cell. Variations in its intensity are probably a result of changes in electrode reflectivity.

According to Griffith,[7] characteristic frequencies for terminal carbonyl groups fall in the range 1900—2100 cm^{-1} while lines due to bridging carbonyl groups appear between 1730 and 1940 cm^{-1}. Therefore, we conclude that the surface carbonyl groups detected are of the terminal type. Assuming that the frequency displacement from the $CHCl_3$ solution value for dissolved CO (2131 cm^{-1})[8] reflects a decrease in force constant, the 2098 cm^{-1} line is characteristic of adsorbed CO which is less 'activated' by adsorption ($\Delta\nu_{CO}$ *ca.* 35 cm^{-1}) than those groups represented by the 2081 cm^{-1} band ($\Delta\nu_{CO}$ *ca.* 50 cm^{-1}). However, these differences are small compared with those expected[7] for different surface co-ordination configurations.

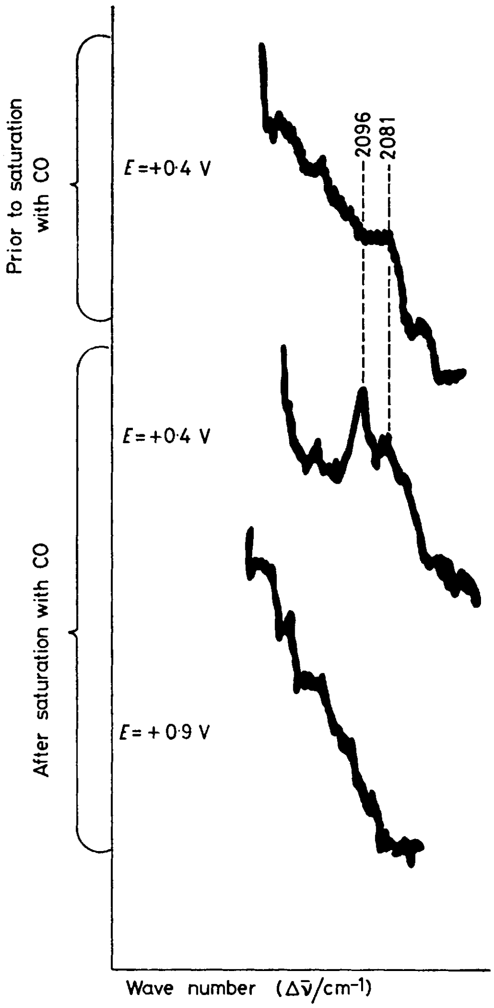

Figure 2. Raman spectra from a grey platinized platinum electrode surface in 1 M H_2SO_4: slits, 10 cm^{-1}; line image, 45° cell (Figure 1b); 100 mW, 514 nm Ar^+; 64-fold average at each stage.

The intensities of the lines observed can be indirectly estimated to be *ca.* 12 counts s^{-1}. This figure may be compared in an 'order of magnitude' estimation involving typical figures derived from 'dry oxide' adsorption spectra recorded in this laboratory. One monolayer of a typical organic adsorbate (*e.g.* an alkene) on Al_2O_3 of surface area 125 m^2 g^{-1} generates, at the instrumental sensitivity of the present study, maximum line intensities of the order of 1250 counts s^{-1} (after laser power and bandpass corrections). The mass specific area of a platinized platinum[3] deposited at 6 mA cm^{-2} is *ca.* 4 m^2 g^{-1}. Simple proportion would then lead one to expect *ca.* 40 counts s^{-1} for a monolayer of a 'typical' adsorbate on a platinized surface of the type used in this study. While this is an imprecise estimate, which ignores the specific parameters of reflectivity, transmission, electrode coverage, surface steric factors, *etc.*, it appears reasonable to conclude that most adsorbates would exhibit spectra of peak intensity < 100 counts s^{-1}. This conclusion is further supported by recent results for adsorbed thiocyanate on a roughened Ag electrode.[9] The extraordinarily intense spectra (2×10^3 counts s^{-1}) detected for the Ag–carboxylate[9,10] system have therefore been recently interpreted[9] in terms of micellar rather than conventional monomolecular layer adsorption at an electrode surface.

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