

Reactions of Organic Monolayers on Carbon Surfaces Observed with Unenhanced Raman Spectroscopy

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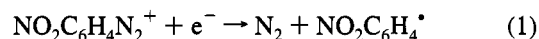
Abstract: High sensitivity surface Raman spectroscopy was used to acquire spectra from monolayers of nitrophenyl groups covalently bonded to glassy carbon (GC) and ordered graphite. 4-Nitrophenyl radical was generated by electroreduction of 4-nitrophenyl diazonium ion in acetonitrile, then the radical covalently bonded to the carbon surface. Raman spectroscopy with a 488 nm laser and a CCD spectrograph revealed spectral features characteristic of the nitrophenyl group. Voltammetry, XPS, and Raman spectroscopic data established that the surface coverage was 6.5×10^{-10} mol/cm² on glassy carbon and 1.6×10^{-10} mol/cm² on the basal plane of highly ordered pyrolytic graphite (HOPG). Electrochemical reduction of the nitrophenyl surface yielded significant spectral changes, perhaps due to formation of an amine. The similarity of the Raman results for modified HOPG and GC surface indicates that the nitrophenyl radical is quite aggressive, apparently attacking both edge plane and basal plane sites.

Introduction

The history of vibrational spectroscopy applied to electrode surfaces has been long and in many cases quite valuable. Several reviews^{1–3} and notable examples^{4–10} illustrate the value of the molecular structural information from vibrational spectroscopy for understanding surface properties and reactivity. The vast majority of efforts in this area has involved metal/gas and metal/liquid interfaces due to the ability to prepare well defined metallic surfaces and the widespread utility of metals in catalysis and materials science. Although carbon surfaces are also economically important and of significant fundamental interest, vibrational spectroscopy has rarely been applied to studying monolayer films on carbon. FTIR has been applied to multilayer films on carbon^{11,12} and to high surface area carbons^{13,14} but has not been successfully applied to monolayers on carbon surfaces. Carbon does not exhibit electromagnetic field enhancement and is not known to support surface enhanced Raman spectroscopy. Thus, surface Raman has been limited so far to resonance enhanced adsorbates or multilayer films. For example, surface resonance Raman has been used to obtain spectra

of metallophthalocyanines on graphite and glassy carbon (GC).^{15,16} We recently reported on surface Raman of resonant and weakly resonant monolayer and submonolayer adsorbates on GC, obtained after improvements in instrumental sensitivity.^{17–19}

The present report extends this general approach to the case of a covalently bonded monolayer film and its reactions. The adsorbate is not expected to be resonance enhanced, and to our knowledge there is no precedent for Raman observation of surface reactions on carbon surfaces. The surface modification is based on reductive formation of nitrophenyl radical from a diazonium derivative, followed by covalent binding to the carbon surface:



Saveant et al. have reported that nitrophenyl diazonium reduction leads to a monolayer film of nitrophenyl groups on carbon and that binding of the nitrophenyl radical is nonselective for basal or edge plane carbon sites.^{20,21} We report here the use of Raman spectroscopy to observe chemisorbed nitrophenyl on GC and highly ordered (HOPG) pyrolytic graphite and spectroscopic observation of the electrochemical reduction of surface nitrophenyl groups.

Experimental Section

Instrumentation. Details of the Raman spectroscopy have been presented in previous reports and are only briefly described here.^{17–19} Raman spectra were acquired with the 488 nm line of an argon ion laser (Coherent Innova 70) with a power of 18 mW at the sample. The

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Raman signals were collected in 180° backscattered geometry by a *f*/1.4 camera lens matched to an *f*/4 monochromator (Chromex 250). A holographic band rejection filter (Notch+, Kaiser Optical Systems) was used in the collimated region of the scattered light. Many spectra were obtained in air at room temperature, but sample resistance to beam damage was significantly improved by cooling the sample with LN₂ in a cell (glass with quartz window) evacuated to 10⁻³ Torr. A cooled CCD (TEK 512 CB/AR, Photometrics CH 260 camera head) was used for detection. Spectra displayed in figures are sums of several integrations (as noted in Figure legends) after spike removal by Photometrics software.

The electrochemical modification of carbon surfaces was performed using a PAR 173 potentiostat. The potentiostat output was monitored using a voltage to frequency converter and a pulse counter so that the total charge passed through the surface could be controlled. A saturated calomel electrode (SCE) was used as the reference electrode and a platinum wire was used as the auxiliary. Electrolysis solutions were 0.1 M tetrabutylammonium tetrafluoroborate (NBu₄BF₄) in acetonitrile (ACN).

Reagents. Tetrabutylammonium tetrafluoroborate and 50% fluoboric acid were obtained from Aldrich Chemical Company. Sodium nitrite and *p*-nitroaniline were from Sigma. The solvents used were reagent grade acetonitrile, ethanol, and ether. 4-Nitrophenyl diazonium tetrafluoroborate was synthesized according to the procedure described by Dunker et al.²² A solution of 18 g sodium nitrite in 60 cc of water was added slowly to a mixture of 32.1 g of *p*-nitroaniline in 115 cc of 50% fluoboric acid cooled in an ice-bath and stirred vigorously. The diazonium salt was collected and washed with fluoboric acid, twice with ethanol, and then thoroughly with ether.

Surface Derivatization. Carbon surfaces were modified by an electrochemical reduction method of Saveant which can be used for the covalent attachment of aromatic groups onto carbon.^{20,21} Glassy carbon (GC-20, Tokai) surfaces were successively polished with 1.0, 0.3, and 0.05 μm alumina (Buehler) on a polishing cloth and subsequently washed and sonicated in nanopure water (Barnstead) for about 10 min and then in acetonitrile (ACN) for another 10 min. Cleaned GC surfaces were used as cathodes in the electrolysis of 4-nitrophenyl diazonium salt at -0.3 V vs SCE in ACN containing 0.1 M NBu₄BF₄, and the reduction charge was monitored. After derivatization, the GC surfaces were rinsed thoroughly in electrolyte and sonicated in acetonitrile for 3 min before Raman spectra were taken. HOPG (Union Carbide, ZYH grade) surfaces were prepared by cleaving the basal plane using adhesive tape. The edge plane of HOPG was obtained by cutting it through with a razor blade to expose a fresh surface. Both basal and edge plane HOPG surfaces were modified using the same procedures as that for GC surfaces. All the modified carbon surfaces were dried with a stream of high-purity Ar gas and then analyzed spectroscopically.

Data Analysis. To avoid sample damage due to excess irradiation, the laser was focused at different spot on the modified surface when each spectrum was taken. The spectra displayed in Figures 1, 2, 6, and 7 represent the average of several different spots on the modified carbon surface as indicated in the legends. The spectrum of the diazonium salt treated GC was acquired first, and then polished GC was acquired under the same conditions. The "subtracted" spectrum was obtained by subtracting the polished GC spectrum from the treated spectrum. In the spectral region covered, glassy carbon has two major bands (~1360 and 1600 cm⁻¹).^{23,24} Because the intensities of these two bands varied slightly from one sample to another, carbon band intensities were adjusted to equal height before subtraction. Spectra of HOPG were analyzed by the same procedures.

Results

Surface Spectra. Raman spectra of the nitrophenyl modified GC surface and untreated GC are shown in Figure 1, spectra A

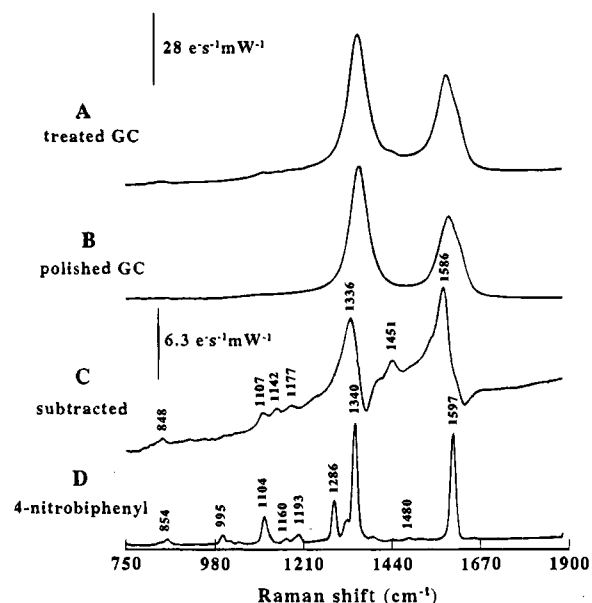


Figure 1. Raman spectra of nitrophenyl modified GC (A) and polished GC (B) obtained with a 488 nm laser and cumulative integration time of 183.3 min (22 spectra of 500 s each were summed). Spectrum C is the difference of A and B, and D is a spectrum of solid 4-nitrobiphenyl. Reduction charge during diazonium reduction was 1.2×10^{-3} Coul/cm².

Table 1. Frequencies for Nitrophenyl Modified Carbon

GC	(HOPG) _{edge}	(HOPG) _{basal}	solid 4-nitrobiphenyl	assignment
848 ^a	850	849	854	NO ₂ bend
			995	phenyl ring
1107 ^a	1108	1109	1104	in-plane
			1160	C-H bend
1142 ^a	1150	1148	1160	in-plane
			1193	C-H bend
1177 ^a	1180	1181	1193	in-plane
			1286	C-H bend
			1286	C-N stretch
1336	1356 ^b	1333	1340	NO ₂ sym stretch
1451 ^a	1444	1450	1480	C-C stretch
1586	1594	1590	1597	C=C stretch

^a Standard deviation of these peak frequencies was ≤ 3 cm⁻¹ for 15 different modified GC surfaces. ^b Carbon "D" band was not completely subtracted in this case.

and B. Subtraction of the untreated GC spectrum yields spectrum C, revealing bands from surface species. The largest surface bands at 1340 and 1597 cm⁻¹ are close to the GC phonons (~1360 and 1600 cm⁻¹), and there is some risk that they could be artifacts of subtraction. However, they were quite reproducible from surface to surface, and there is a distinct band shift to lower Raman shift upon subtraction. For 15 modified GC samples observed under the conditions of Figure 1, all modes listed were observed consistently, with most (848, 1107, 1142, 1177, 1451 cm⁻¹) having a standard deviation in peak frequency of 3 cm⁻¹ or less. A spectrum of the model compound 4-nitrobiphenyl is shown in Figure 1D, and its peak frequencies are listed in Table 1, along with those of the surface features from spectrum 1C.

Spectra resulting from diazonium modification of basal and edge plane highly ordered pyrolytic graphite (HOPG) are shown in Figure 2 and Table 1. The absence of the 1360 cm⁻¹ "D" phonon in HOPG²⁴ simplifies the carbon spectrum and produces a lower background in the spectrum of modified surfaces. The surface spectrum of Figure 2C exhibits several features similar to those on GC. The 1333 cm⁻¹ band of Figure 2C did not shift in frequency with 458 nm laser light and was not observed

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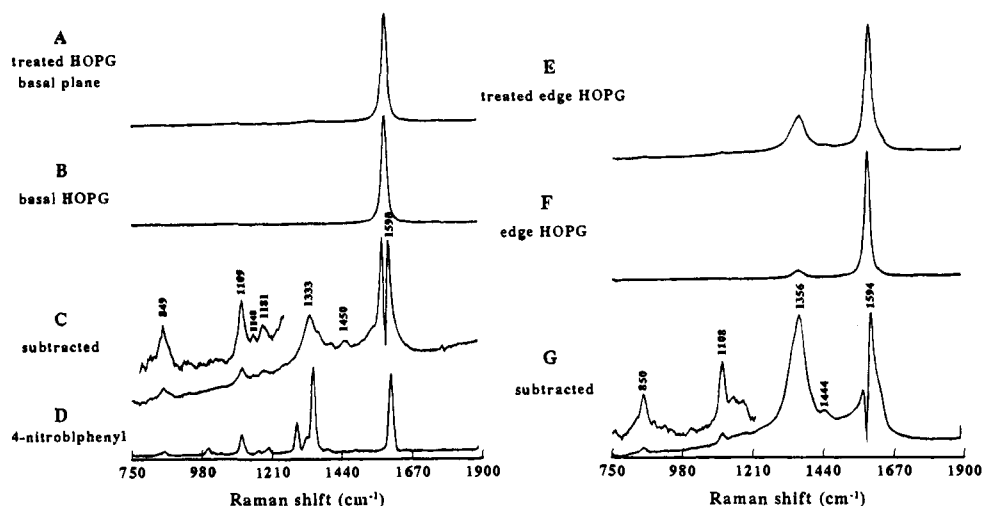


Figure 2. Raman spectra of HOPG basal plane before (B) and after (A) nitrophenyl derivatization, with the difference (A - B) shown as spectrum C. Spectrum E is derivatized edge plane HOPG, F is untreated edge plane HOPG, and G is their difference (E - F). Cumulative integration time for each of spectra A, B, E, and F was 140 min.

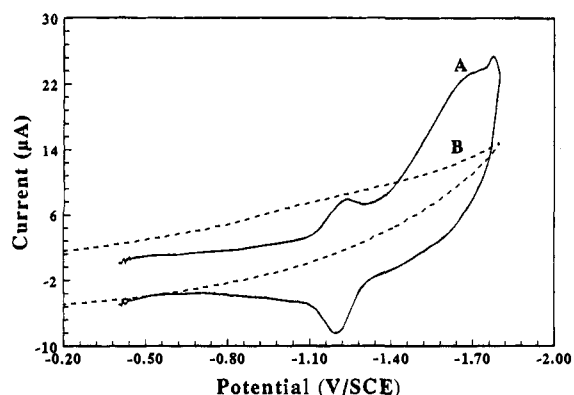


Figure 3. Voltammogram of nitrophenyl modified GC in 0.1 M NBu₄-BF₄ in acetonitrile (A) and background electrolyte (B). Scan rate = 0.2 v/s. The nitrophenyl surface was prepared by electrolysis of 1 mM 4-nitrophenyl diazonium ion.

with 784 nm light. Since the "D" band of disordered carbon shifts with laser wavelength²³ and is not observable on modified HOPG with a 784 nm laser, the 1333 cm⁻¹ band of spectrum 2C is *not* attributable to disordering of the HOPG during derivatization. The modified HOPG edge spectrum (Figure 2G) shows features similar to those of basal HOPG, but the 1356 cm⁻¹ band is more intense than the 1333 cm⁻¹ band observed on the basal plane.

Surface Coverage. Before considering the vibrational spectra further, it is important to establish the surface coverage of nitrophenyl groups on the GC surface. Several methods were employed to determine surface coverage, with the results summarized in Table 2. Voltammetry of the modified GC surface in acetonitrile, shown in Figure 3, exhibited a surface wave for reduction of the nitro group to the radical anion at ca. -1.2 V vs SCE. Integration of the reduction peak yielded 6.5×10^{-10} mol/cm², based on the geometric electrode area. The XPS spectrum of a nitrophenyl modified GC surface is shown in Figure 4, with the N_{1s} region magnified (inset). The lower energy N_{1s} band at 400 eV is present in polished unmodified GC and is not attributable to nitrophenyl modification. The higher energy N_{1s} peak (406 eV) corresponds to that of nitrogen in a nitro group. The area ratio of N_{1s}/C_{1s} after correction for instrumental sensitivity is 5.5 atom%. If one assumes the simplest case of a carbon atom surface density equal to that of basal plane graphite (7.3×10^{-9} mol/cm²), the XPS results yield an NO₂ coverage of 4.3×10^{-10} mol/cm².

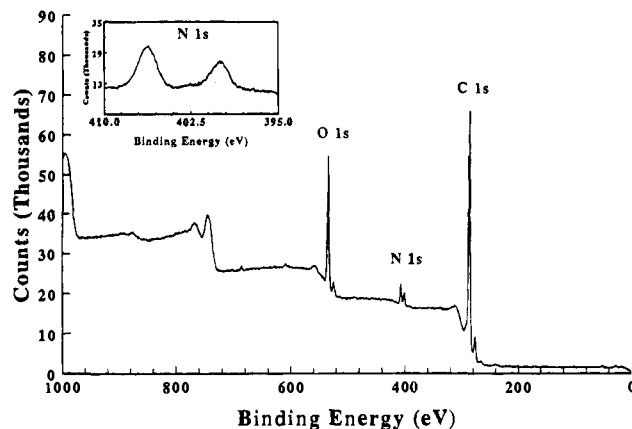


Figure 4. Survey XPS spectrum of nitrophenyl modified GC, with magnified inset of the N_{1s} region.

Table 2. Surface Coverage of Nitrophenyl^a

method	surface coverage (mol/cm ²)
integration of the voltammetric signal of 4-nitrophenyl group on GC	$6.5 \pm 0.5 \times 10^{-10}$ ($N = 4$) ^b
XPS N/C ratio on GC	4.3×10^{-10}
Saveant et al. ²⁰	14×10^{-10}
Raman ^c on GC	28×10^{-10}
HOPG CV	1.6×10^{-10}
HOPG Raman ^c	12×10^{-10}
predicted for close packing	12×10^{-10}

^a 4-Nitrophenyl diazonium ion (1 mM), 10 min electrolysis time. ^b Based on geometric area, and a 1e⁻ reduction to nitrophenyl anion. N is the number of modified surfaces averaged. ^c Assuming a cross section equal to that of nitrophenyl. The cross section number density product (βD) of GC at 488 nm was assumed to be 1.3×10^{-10} sr⁻¹. For HOPG, βD assumed to equal 4×10^{-11} sr⁻¹.

The Raman cross section of the 1107 cm⁻¹ band of nitrophenyl was determined by comparison to the cross section of the 992 cm⁻¹ band of benzene²⁵ to be 1.6×10^{-28} cm² molecules⁻¹ sr⁻¹ (Table 3). Assuming that surface bound 4-nitrophenyl has the same cross section as nitrophenyl, the surface coverage of nitrophenyl may be estimated from the observed 1107 cm⁻¹ peak area, using the GC 1360 cm⁻¹ band as an internal standard.¹⁹ The observed Raman 1107 cm⁻¹ band area yields a surface coverage estimate of 28×10^{-10} mole/cm².

The intensity of the 1107 cm⁻¹ surface band was monitored as a function of the charge passed during deposition of the

Table 3. Cross Sections for Model Compounds in Solution

Raman band	laser wavelength (nm)	cross section (cm ² molecule ⁻¹ sr ⁻¹)	relative value
C ₆ H ₆ (992 cm ⁻¹) ^a	488 nm	3.25 × 10 ⁻²⁹	1
C ₆ H ₅ NO ₂ (1345 cm ⁻¹)	488 nm	10.3 × 10 ⁻²⁹	3.2
C ₁₂ H ₉ NO ₂ (1341 cm ⁻¹)	488 nm	61 × 10 ⁻²⁹	19
C ₁₂ H ₉ NO ₂ (1107 cm ⁻¹)	488 nm	16 × 10 ⁻²⁹	5

^a From ref 25, remaining cross sections determined by comparison to the benzene 992 cm⁻¹ band.

Table 4. Observed Raman Frequencies

nitrophenyl modified GC	reduced GC	nitrophenyl HOPG _{basal}	reduced HOPG _{basal}	aminobiphenyl
848		849		
	925		921	996
				1042
1107		1109		
1142	1146	1148	1148	1159
1177		1181		
	1193		1192	1195
				1286
1336		1333		
1451	1449	1450	1447	
				1524
1586	1594	1590	1591	1599

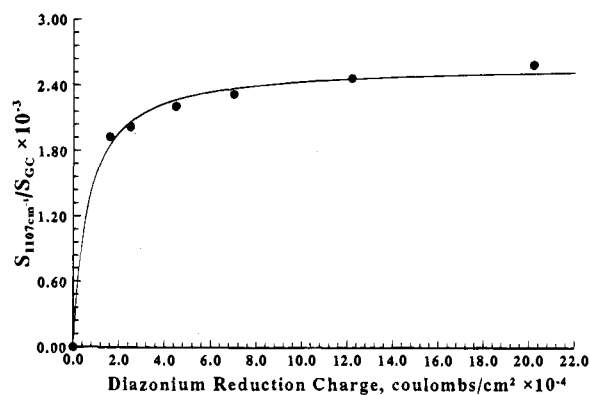


Figure 5. Intensity of the 1107 cm⁻¹ band of surface nitrophenyl on GC (stated as a peak area ratio relative to the 1580 cm⁻¹ carbon phonon) as a function of reduction charge during derivatization, in C/cm². Reduction of 4-nitrophenyl diazonium ion was carried out coulometrically at -0.3 V vs SCE. Line is a fit to a Langmuir isotherm, with *R*² = 0.99.

nitrophenyl modifier. Since each molecule of diazonium reduced by 1e⁻ produces a nitrophenyl radical, one would expect the surface to saturate soon after a monolayer equivalent of charge has passed during deposition. Figure 5 shows a plot of the 1107 cm⁻¹ peak area vs deposition charge. The signal to noise ratio did not permit accurate determination of peak area below 1 × 10⁻⁴ Coul/cm², but it was observed that the intensity increased slowly after this point. 1 × 10⁻⁴ Coul/cm² is ca. 1 × 10⁻⁹ mol/cm² of e⁻, roughly equal to the stoichiometry expected if each electrogenerated nitrophenyl radical reacts with the surface until saturation is reached.

The theoretical coverage of nitrophenyl groups was calculated with the Hyperchem Molecular Simulation program (Autodesk, Inc.) for the case of close packing on a flat surface. Based on Van der Waals radii, the area of a nitrophenyl group bonded at the edge of the phenyl ring is 13.9 Å² or 12 × 10⁻¹⁰ mol/cm² for ideal close packing. This predicted value is included in Table 2.

In acetonitrile, and the conditions of Figure 3, the surface nitrophenyl group reduces by one electron, yielding an anion radical.²⁰ However, reduction at -1.5 V vs Ag/AgCl in 0.1 M

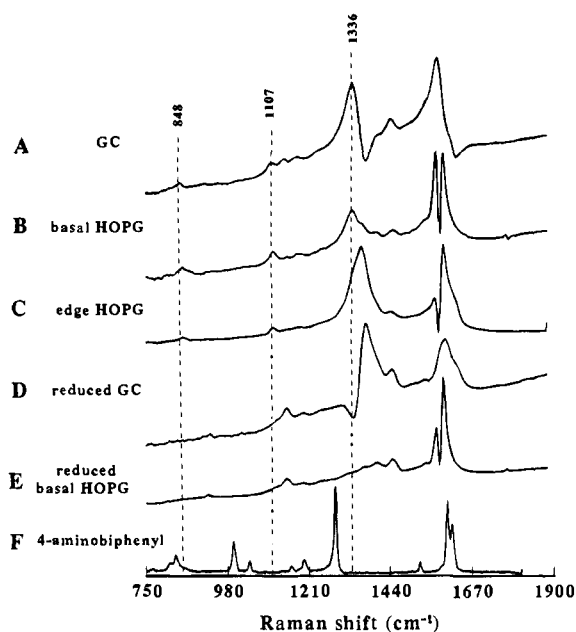


Figure 6. Spectra of modified carbon surfaces following subtraction of the substrate spectrum. Spectra A–C are nitrophenyl modified GC (A) basal plane HOPG (B) and edge plane HOPG (C), while D and E are similar spectra after electrochemical reduction at -1.5 V Ag/AgCl in 0.1 KCl (10% EtOH/H₂O), for GC (D) and basal plane HOPG (E). (F) is a reference spectrum of solid 4-aminobiphenyl.

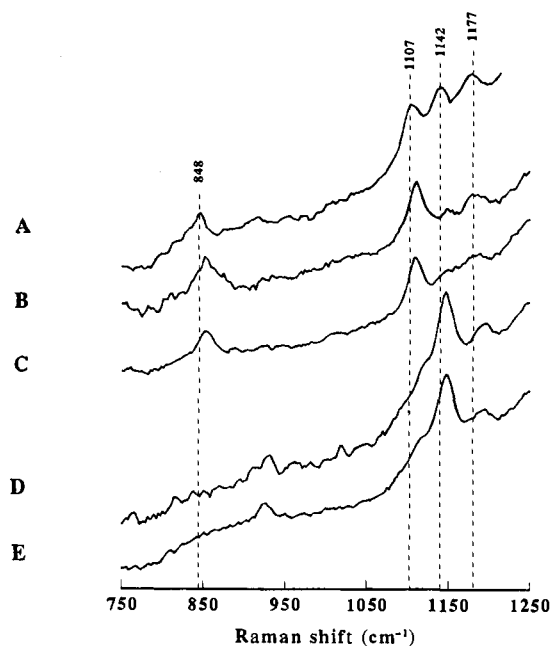


Figure 7. Spectra of Figure 6, expanded in the 750–1250 cm⁻¹ range.

KCl in 10% EtOH/H₂O should reduce the nitro group by 6e⁻ to an amine group,²⁶ yielding an aminophenyl modified surface. Figure 6 compares spectra of the nitrophenyl modified GC and HOPG surfaces with those following reduction in EtOH/H₂O after subtraction of the substrate spectrum. The 848, 1108, and 1336 cm⁻¹ bands present in spectra of the nitrophenyl modified GC and HOPG are removed by reduction, the 1142, 1177, and 1586 cm⁻¹ bands remain, and a 925 cm⁻¹ band appears. Figure 7 is an expanded view of the 750–1250 cm⁻¹ range of Figure 6, showing significant differences in the 1107–1177 cm⁻¹ bands for the various surfaces.

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Discussion

Based on the surface coverage data listed in Table 2, the Raman spectrum of Figure 1C is that of an approximately monolayer film of nitrophenyl groups on glassy carbon. As noted elsewhere, it is more difficult to obtain unenhanced Raman spectra on carbon than on metal surfaces because of the relatively high inelastic background from carbon, particularly in the region of the sp^2 carbon phonons at 1360 and 1580 cm^{-1} .^{18,19} The shot noise from carbon background degrades the signal to noise ratio (SNR) of the adsorbate bands, thus requiring a more sensitive spectrometer to acquire useful spectra. The surface modes observed in Figure 1C are reproducible and respond to surface chemical changes such as the reduction of the nitro group.

4-Nitrobiphenyl was chosen as a model compound for the nitrophenyl radical covalently bonded to an aromatic ring in the sp^2 carbon matrix. 4-Nitrobiphenyl exhibits most of the bands observed for nitrophenyl modified GC, including 854, 1104, 1160, 1193, 1340, and 1597 cm^{-1} . In most cases, the observed nitrophenyl adsorbate bands are downshifted by 2–15 cm^{-1} relative to 4-nitrobiphenyl. Reduction of nitrophenyl diazonium ion at basal plane HOPG yields surface Raman spectra which are similar to modified GC, except for the absence of the "D" band common in disordered carbon ($\sim 1360\text{ cm}^{-1}$). The absence of "D" band interference permits the 1333 cm^{-1} adsorbate band to be observed more clearly. Note also (Figure 7) that this band is removed by reduction of the modified HOPG surface, implying that it is related to the nitro group and not to the substrate. Nitrophenyl modification of edge plane HOPG also yields similar Raman features, with the expected more intense "D" band. Given the wide range of edge plane density on GC, basal HOPG, and edge plane HOPG, the similarity of the surface Raman spectra is somewhat surprising, since one would expect fewer binding sites on the basal surface. As suggested initially by Saveant et al. the nitrophenyl radical is apparently aggressive enough to bind to both edge and basal sites.²⁰ A more quantitative evaluation of this issue is provided by surface coverage data.

For the derivatization of GC, the results of Table 2 and Figure 5 support the conclusion that the nitrophenyl reagent forms a monolayer. The surface saturates after about 10^{-9} mol of charge/ cm^2 have passed during derivatization, and XPS and voltammetric measurements indicate that roughly half of the electrogenerated nitrophenyl radicals covalently bonded to the GC surface. Raman estimates of coverage are less reliable since they assume the nitrophenyl/GC cross section is the same as nitrobiphenyl, and they lead to higher estimates of surface coverage than voltammetry. However, the coverage determined by both voltammetry and Raman is significantly lower for basal plane HOPG than for GC. Of the approximate factor of 4 difference in the voltammetry results, a factor of 2 may be caused by surface roughness,²⁷ implying that the coverage is about a factor of 2 higher on GC than an HOPG per unit of microscopic area. The edge plane density on HOPG from defects is a few percent,^{28,29} implying that the nitrophenyl coverage is much greater than predicted for HOPG if nitrophenyl attacked only edge sites. Thus the coverage results are

consistent with nitrophenyl attack at both edge and basal sites. It is also possible that the radical attacks edges initially, and then more edge sites are created as the carbon lattice is damaged. By either route, the end result is a coverage of nitrophenyl on basal plane HOPG which is greater than the initial edge plane density.

The reduction of the nitrophenyl derivatized surfaces, shown in Figures 6 and 7 and Table 4, clearly indicate the ability of unenhanced Raman spectroscopy to monitor surface reactions at the monolayer level. The most obvious spectral changes upon reduction of the nitrophenyl surface are loss of the 848, 1107, and 1333 cm^{-1} features and gain of a small 925 cm^{-1} band. The reduced spectra (Figures 6B and 7B) do not obviously resemble that of 4 aminobiphenyl, a model compound for the expected aminophenyl reduction product. Although there is no doubt that the surface has been chemically altered by reduction, it is not certain from the Raman spectra that an aminophenyl surface is the result.

The possibility of modest resonance enhancement of the surface nitrophenyl should be considered, in light of the observation that the Raman intensity is about four times higher than predicted from the nitrobiphenyl cross section (Table 2). Nitrobenzene and nitrobiphenyl are weakly resonance enhanced at 488 nm (if at all), but there may be some increase in cross section when nitrophenyl is bonded to the large graphitic π system. An estimate of the surface nitrophenyl cross section based on the voltammetric surface coverage and observed 1107 cm^{-1} surface Raman intensity yields a value about four times that of the 1107 cm^{-1} band of nitrobiphenyl. If enhancement is occurring at all when the nitrophenyl group bonds to the carbon surface, it is less than a factor of 10, and very much smaller than the factors of 10^3 – 10^5 for resonance Raman active species^{18,19} or the 10^3 – 10^4 factors common to electromagnetic field enhancement.^{3,6}

Assignments. Band assignments for the nitrophenyl modified carbon are summarized in Table 1. An NO_2 bending mode common to nitrobenzene and nitrobiphenyl is 848 cm^{-1} .^{30,31} It disappears upon NO_2 reduction, as expected. The 995 cm^{-1} band of nitrobiphenyl is assigned to the monosubstituted benzene ring. It is not observed in para-disubstituted benzenes³¹ and is therefore not observed on the nitrophenyl surface. The 1107, 1142, and 1177 cm^{-1} modes are likely to be in plane aromatic C–H deformations, possibly coupled to the NO_2 group. At least one of these (1107 cm^{-1}) decreases significantly in intensity upon reduction, possibly because it involves the NO_2 group. The 1336 cm^{-1} is close to the NO_2 symmetric stretch observed in nitrobiphenyl and nitrobenzene, and its disappearance upon reduction strongly associates it with the NO_2 group. The 1586 cm^{-1} band is assigned to an aromatic ring deformation involving a C=C stretch. The 1451 cm^{-1} assignment is uncertain, but it may involve either the nitrophenyl ring itself or the C–C bond between the ring and the carbon surface.

Although there are some similarities, these assignments should not be confused with the dinitrophenylhydrazine modified surface reported previously.¹⁷ The DNPH/GC adduct is strongly resonance enhanced, and its Raman spectrum is dominated by vibrations coupled to the C–N–N–C chromophore. In particular, the NO_2 stretch of the DNPH/GC adduct is not resonance enhanced, and the 1330 cm^{-1} mode observed for that case was assigned to nitrophenyl ring deformation.

The current results clearly establish that informative Raman spectra may be acquired for monolayer organic species chemisorbed to carbon surfaces, in the absence of known enhancement mechanisms. Furthermore, electrochemical modification of the monolayer can be observed spectrally, leading to major changes

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in the vibrational spectrum. The results also lead to two potentially important issues which we plan to address further with isotopic substitution of the modified surface. First, do the differences in the nitrophenyl spectra on different carbon surfaces (Figures 6 and 7) reveal specific details about the binding sites on the carbon? In particular, can the structure of particular sites on the surface be inferred from the Raman spectra? Second, can spectral changes accompanying reduction reveal the products or intermediates of the electrochemical

reduction of surface bound nitrophenyl? These questions are currently under investigation.

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