Raman Spectroscopic Determination of the Structure and Orientation of Organic Monolayers Chemisorbed on Carbon Electrode Surfaces

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Azobenzene (AB) and 4-nitroazobenzene (NAB) were covalently bonded to carbon surfaces by electrochemical reduction of their diazonium derivatives. The N_{1s} features of XPS spectra of modified surfaces had intensities expected for monolayer coverage. However, the Raman spectra were significantly more intense than expected, implying an increase in scattering cross section upon chemisorption. A likely explanation is resonance enhancement of the carbon/adsorbate chromophore analogous to that reported earlier for dinitrophenylhydrazine (DNPH) chemisorption. Vibrational assignments indicate that the C−C vibration between azobenzene and the carbon surface is in the $1240−1280$ cm^{-1} region, and this conclusion is supported by spectra obtained from [^{13}C]graphite. Observation of depolarization ratios for 4-nitroazobenzene and DNPH on graphite edge plane indicate that NAB is able to rotate about the NAB/carbon C−C bond, while chemisorbed DNPH is not. The partial multiple bond character of the DNPH linkage to graphite is consistent with the observation that the DNPH π system remains parallel to the graphitic planes.

In the continuing and widespread effort to relate the structure of electrode surfaces to their electron transfer reactivity, a wide variety of surface structural probes and surface modification techniques have been employed. Major progress has been made in these regards for metal electrode surfaces, due in large part to the ability to prepare clean, ordered metal surfaces and the availability of surface characterization techniques such as XPS, FT-IR, and surface-enhanced Raman spectroscopy (SERS), to name a few. Despite their practical importance and industrial utility, common carbon electrode surfaces such as graphite and glassy carbon are much less well understood than metals, and the bases of reactivity at carbon surfaces are often unknown or obscure. Carbon surfaces can behave quite differently from metals, due to the presence of functional groups, the anisotropy of the sp^2 carbon lattice, the extended π system in the graphitic planes, and the differences in electronic properties manifested in conductivity and optical constants.[1−5] Carbon's optical properties,

particularly its strong absorptivity in the UV−visible−IR regions and its inability to support electromagnetic field (EM) enhancement for SERS, make it much less amenable than metals to surface spectroscopy.[6] FT-IR of monolayer or submonolayer adsorbates on carbon electrodes has not been reported, and Raman spectra of adsorbates which do not exhibit strong resonance enhancement have only been reported recently.[7] While there is great practical and fundamental interest in relating the surface structure of carbon to its electrochemical reactivity, efforts toward this end have been frustrated by the lack of molecular information about carbon surfaces.

Our goal in the present work is to extend Raman spectroscopy for characterizing carbon surfaces. We recently reported the observation of physisorbed and chemisorbed monolayers and submonolayers on glassy carbon surfaces in the absence of significant resonance or EM field enhancement.[8] Of particular interest is the effect of graphitic carbon's anisotropy, functional groups, and electronic structure on the vibrational spectrum and orientation of adsorbates. In the current report, we exploit the sensitivity and polarization properties of unenhanced Raman spectroscopy to provide structural information about chemisorbed adsorbates derived from diphenylhydrazine (DNPH) and 4-nitro-azobenzene (NAB).

EXPERIMENTAL SECTION

Reagents. 4-(4-Nitrophenylazo)aniline, 4-nitroazobenzene, tetrabutylammonium tetrafluoroborate, and 50% fluoboric acid were obtained from Aldrich Chemical Co. The solvents used were reagent grade acetonitrile, ethanol, and ether. 4-Nitroazobenzene-4′-diazonium tetrafluoroborate was synthesized from 4-(4-nitrophenylazo)aniline, according to the procedures described by Dunker et al.[9] 2,4-Dinitrophenylhydrazine (DNPH) was used as purchased (J. T. Baker) in a 10 mM solution with 1% HCl (J. T. Baker) in absolute ethanol (McCormick Distilling Co., Inc.), as described elsewhere.[10]

Glassy carbon (Tokai GC-20) was prepared by polishing on a Buehler microcloth using successive 1.0, 0.3, and 0.05 μm alumina particles (Buehler) slurried in Nanopure (Barnstead) water. Polished GC was then sonicated and rinsed between polishing

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steps with Nanopure water to remove any debris. The edge plane of highly ordered pyrolytic graphite (HOPG) was prepared by fracturing a 10 mm × 10 mm × 0.5 mm HOPG piece; the fresh HOPG edge surface was then rinsed with either acetonitrile or absolute ethanol before any surface derivatization.

Procedures. The 4-nitroazobenzene-modified surface was obtained by electrochemical reduction of 4-nitroazobenzene-4′-diazonium tetrafluoroborate (1 mM) at −0.5 V vs SCE in acetonitrile containing 0.1 M NBu_4BF_4. The derivatization method has been described by Saveant et al.[11,12] and can be used for the covalent attachment of aromatic groups onto carbon surfaces. After derivatization, surfaces were sonicated in acetonitrile for 5 min before Raman spectra were acquired. In the case of HOPG, modified surfaces were thoroughly rinsed with CH_3CN, but not sonicated, in order to avoid mechanical damage. Identical procedures were employed to prepare 4-azobenzenediazonium tetrafluoroborate and to chemisorb azobenzene. DNPH treatment followed the procedures described by Fryling et al.,[10] with a final treatment for 10 min in 0.1 M KOH/ethanol. Carbon surfaces were immersed in absolute ethanol overnight after DNPH treatment. They were then dried in a stream of purified argon before Raman analysis.

Instrumentation. The Raman spectrometer was similar to that described previously[10,13] but with some improvements to increase the signal-to-noise ratio. A 180° backscattered geometry with a 50 mm, f/1.4 focusing and collection lens preceded a Kaiser "Holospec" f/1.8 spectrograph. The fixed grating and back-thinned CCD detector resulted in a 600−1800 cm^{-1} Raman shift range relative to the 514.5 nm laser line. Polarization measurements were implemented as described previously,[14] with a polarization analyzer and scrambler positioned in the collimated collection beam preceding the spectrograph. Spectrometer response to parallel and perpendicular polarized light was calibrated as before[14] and verified by measuring depolarization ratios for benzene and CCl_4. Uppercase X, Y, and Z refer to the incident laser coordinates, with the light always polarized parallel to Y. Lowercase a, b, and c refer to the graphite coordinate axes, with the c-axis perpendicular to the graphitic planes. The 180° backscattered depolarization ratio, ρ_Z, is defined as $I_\perp/I_\parallel$, referenced to the incident light.[14,15]

RESULTS AND DISCUSSION

Surface Spectra and Cross Sections. Chemisorbed 4-nitroazobenzene and DNPH were chosen for this study because of major differences in their spectroscopy and in their expected bonding to the carbon surface. Reduction of 4-nitroazobenzene-4′-diazonium is expected to yield a 4-nitroazobenzene-modified surface with a carbon−carbon single bond to the graphitic surface. Figure 1 shows Raman spectra of polished GC20 before (Figure 1B) and after (Figure 1A) reduction of the diazonium salt in acetonitrile. Subtraction of the GC spectrum yields Figure 1C, which has many similarities to the spectrum of solid NAB (Figure 1D). Note that the surface peaks are quite strong, due to an increase in cross section upon chemisorption (see below). Figure
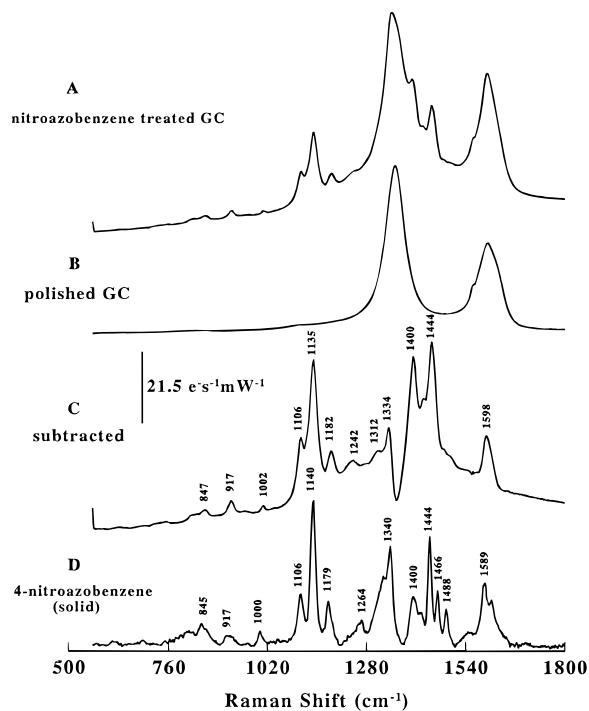
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Figure 1. Raman spectra of polished GC 20 before (B) and after (A) electrochemical reduction of 4-nitroazobenzene-4′-diazonium. Integration time was 10 min, 50 mW at sample. Spectrum C is the difference spectrum (A − B), and spectrum D is that of solid 4-nitroazobenzene.
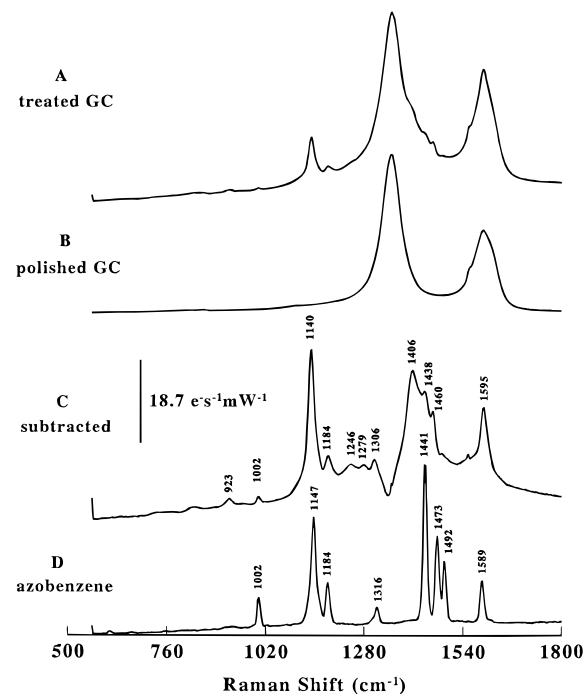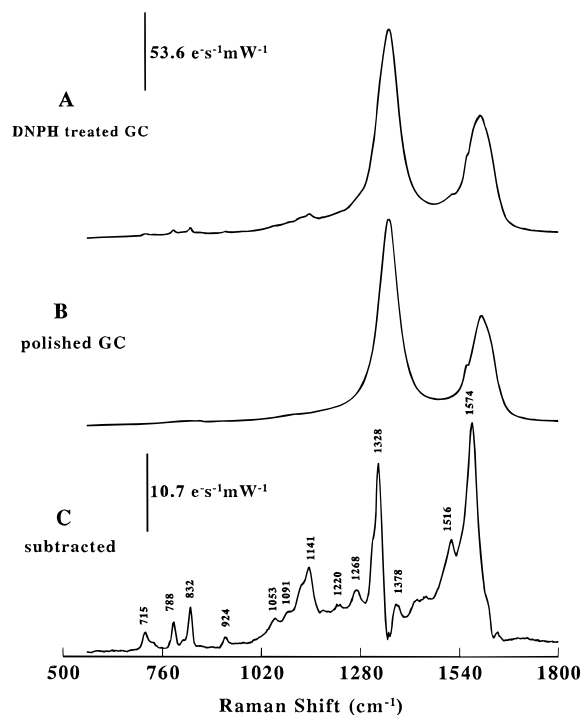

Figure 2. Same as Figure 1, but for the reduction of 4-azobenzenediazonium. Integration time was 10 min for spectra A and B.

2 shows analogous spectra for chemisorbed azobenzene prepared by reduction of 4-azobenzenediazonium in 0.1 M NBu_4BF_4 in CH_3CN at a GC 20 electrode. Raman spectra of polished GC before and after DNPH treatment are shown in Figure 3. DNPH chemisorbs to surface carbonyl groups to form a C−N−N−C linkage which is resonance enhanced.[10] The surface coverage of the DNPH adduct equals the initial surface carbonyl coverage, generally 1−10%. The subtracted spectrum in Figure 3C differs

Figure 3. Raman spectra of polished GC before (B) and after (A) DNPH treatment and the difference spectrum (C). Integration time was 10 min, 50 mW at sample.
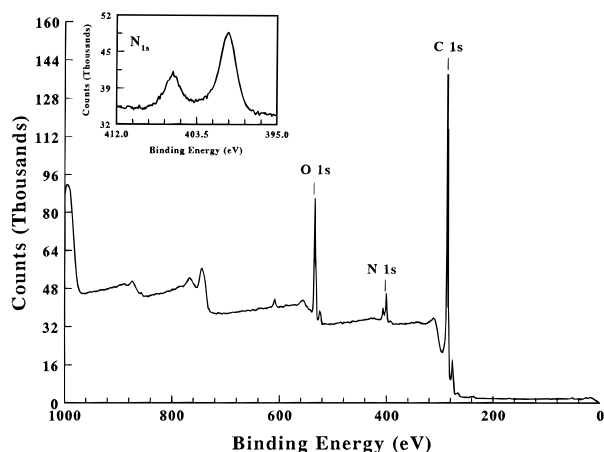

Figure 4. Survey and high-resolution (inset) XPS spectra of chemisorbed 4-nitroazobenzene on GC 20.

in appearance from that reported previously[10] due to the wider spectral coverage and the use of 514.5 rather than 488.0 nm excitation. In addition, the S/N ratio in the current work is higher due to the use of a more efficient spectrograph.

Figure 4 shows the XPS survey spectra of a 4-nitroazobenzene-modified GC surface and the magnified N_{1s} region (inset). The signals observed at 400 and 406 eV correspond to the azo and the nitro groups, respectively. The diazonium peak at 402 eV disappeared after modification, indicating that any physisorbed diazonium salt was not observable. The surface coverage of the modifying layer was estimated through the integration of nitrogen peak areas and comparison of them with the C_{1s} peak area. After instrumental sensitivity correction, the estimated surface coverage of 4-nitroazobenzene on the GC surface is 1.4×10^{-10} mol/cm^2. Electrochemical determination of the NAB coverage failed due to poorly defined voltammetric peaks. However, chemisorbed azobenzene yielded a well-defined reduction peak in acetone at

-1.36 V vs SCE. Assuming a 1e$^-$ reduction, this peak yielded an azobenzene coverage of 3.5×10^{-10} mol/cm^2 on polished GC 20. The Hyperchem molecular simulation program (Autodesk, Inc.) was also used to calculate the theoretical monolayer coverage of 4-nitroazobenzene on a carbon surface. For a compact 4-nitroazobenzene monolayer, theoretical monolayer coverage can be up to 10×10^{-10} mol/cm^2. Therefore, the 4-nitroazobenzene-modified GC surface coverage is in the monolayer region, but not as high as the 4.3×10^{-10} mol/cm^2 reported for chemisorbed nitrophenyl groups.[8]

The Raman cross section for solution phase 4-nitroazobenzene (dissolved in benzene) was determined by comparing the peak area of the NAB 1135 cm^{-1} band to that of the benzene 992 cm^{-1} band, whose cross section is known.[7] The same instrumental parameters and geometry were used for both samples, and the peak areas were adjusted for sample number density. The cross section of the 1135 cm^{-1} band of solution phase NAB was 19 times that of the benzene 992 cm^{-1} band and equaled 5.4×10^{-28} cm^2 molecule^{-1} sr^{-1}. The cross section of the chemisorbed NAB was also determined by comparison to the glassy carbon 1360 cm^{-1} peak area, taking into account the Raman sampling depth in GC.[7] Using the XPS coverage of 1.4×10^{-10} mol/cm^2 for NAB, the 1135 cm^{-1} cross section for chemisorbed NAB was 1640 times that of the solution species. Even if the surface coverage were in error by a factor of 10, the chemisorbed NAB has a much larger cross section than the solution species. A likely explanation is a strong electronic interaction between the NAB and graphitic π system, causing either an increase in polarizability or a shift in absorption maximum toward 515 nm, or both.

Assignments. The assignment of the surface Raman bands for DNPH chemisorbed to GC has been discussed in detail previously,[10] with the three main bands being assigned to the N−N stretch ($\sim$1140 cm^{-1}), nitrophenyl ring deformation combined with NO$_2$ stretch ($\sim$1330 cm^{-1}), and C−N−N−C stretch ($\sim$1600 cm^{-1}). The surface Raman bands for chemisorbed 4-nitroazobenzene were assigned in the current work by a comparison to literature assignments,[16−19] spectra of solid NAB, and calculations from the molecular mechanics program Cerius.[2] The frequencies and assignments are listed in Table 1. The spectra of both chemisorbed NAB and AB exhibit strong bands in three regions, 1135−1150, 1400−1450, and 1580−1600 cm^{-1}. An $\sim$1135 cm^{-1} band was also observed for chemisorbed nitrophenyl and chemisorbed DNPH and assigned to the C−H bends on the phenyl rings. The bands in the range 1400−1450 cm^{-1} were observed for both chemisorbed NAB and AB, indicating that they cannot be due solely to the NO$_2$ stretch, which normally occurs at lower frequency ($\sim$1340 cm^{-1}). Several bands are observed in the same region for solid NAB and AB, and the 1441 cm^{-1} band of azobenzene has been assigned to the N=N stretch (16−19). The 1580−1600 cm^{-1} bands are consistent with phenyl ring deformation involving C=C stretches. All of the materials in Table 1 would be expected to exhibit such bands, chemisorbed or not.

Molecular mechanics calculations were carried out on both NAB and a model compound, 4-phenyl-4′-nitroazobenzene (PNAB).

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Table 1. Frequencies (cm⁻¹) and Assignments for Azobenzene Derivatives

chemisorbed		solid		Cerius[2]	
NAB	AB	NAB	AB	calculation[a]	assignment
847, w[b]		845		802, w, 45[c]	NO₂ bend
917, w	923, w	917		891, w, 48	C−H bend
1002, w	1002, m	1000	1002	1000, w,54	ring deformation
1135 ,s	1140 ,s	1140	1147	1117, s,69	phenyl−N stretch
1182, m	1184, m	1179	1184	1175, w, 72	C−H bend
1242, w	1246, 1279, w			1241, w, 78	C−C stretch
1334, m		1340		1206, m, 77	NO₂ stretch
1400, s	1406, s	1400		1398, m, 84[d]	N=N stretch
1444, s	1460, w	1444	1441	1488, vs, 88[d]	N=N stretch
1598, m-s	1595	1589	1589	1581, s, 94	phenyl C=C stretch

a Calculated for 4-phenyl-4′-nitroazobenzene. *b* w, weak; m, medium; s, strong. *c* Mode number, shown in Figure 5. *d* Mode assignments for the N=N stretch based on the 3-21G basis set have been challenged in the literature[20] and should be considered tentative.

Table 2. Observed and Calculated Frequencies (cm⁻¹) for AB Derivatives

solid AB		[¹²C]phenyl	[¹³C]phenyl[b]
obsd	calcd[a]	AB, calcd	AB, calcd
1002	985, w	986	986
1147	1116, s	1117	1117
1184	1175, w	1178	1178
1241	1224		
1441	1443, m	1488	1489
1473	1479, m		
1492	1500, vs		
1589	1578, m	1581	1581

a Frequency, relative intensity, and mode number. *b* The carbons in the monosubstituted phenyl ring were substituted with ¹³C, to mimic [¹³C]graphite.

The latter structure was chosen to mimic chemisorbed NAB by adding an aromatic substituent in place of the graphite surface. The Gaussian routine of Cerius[2] (Biosym Molecular Simulations, San Diego, CA) calculates both IR and Raman frequencies and predicts relative intensities. The calculation used the HF method of Cerius[2] with the 3-21G basis set. This procedure was shown recently[20] to yield incorrect assignments for modes dominated by the azo stretch, so deductions about modes associated with the N=N bond in azobenzenes should be made carefully. The assignments in Table 1 were based on experimental spectra of analogs of chemisorbed NAB[16−19] as well as the Cerius calculations. Calculated spectra for PNAB showed three strong bands (1117, 1488, and 1581 cm⁻¹), approximately corresponding to those observed for chemisorbed NAB. The accuracy of the calculation was assessed by comparing predicted and observed frequencies for free NAB and AB, with the results listed in Table 2. Although relative intensities are approximate, the calculated frequencies are generally within 5% of the observed values.

The assignments of the main bands of chemisorbed NAB and AB at 1135, 1444, and 1598 cm⁻¹ as the C−N, N=N, and phenyl C=C stretches, respectively, is consistent with the available literature for nonchemisorbed analogs.[16−19] In addition, the 847 and 1334 cm⁻¹ modes associated with the NO₂ group are present in chemisorbed NAB but absent in AB or chemisorbed AB. Both

(20) Armstrong, D. R.; Clarkson, J.; Smith, W. E. *J. Phys. Chem.* **1995**, *99*, 17825.
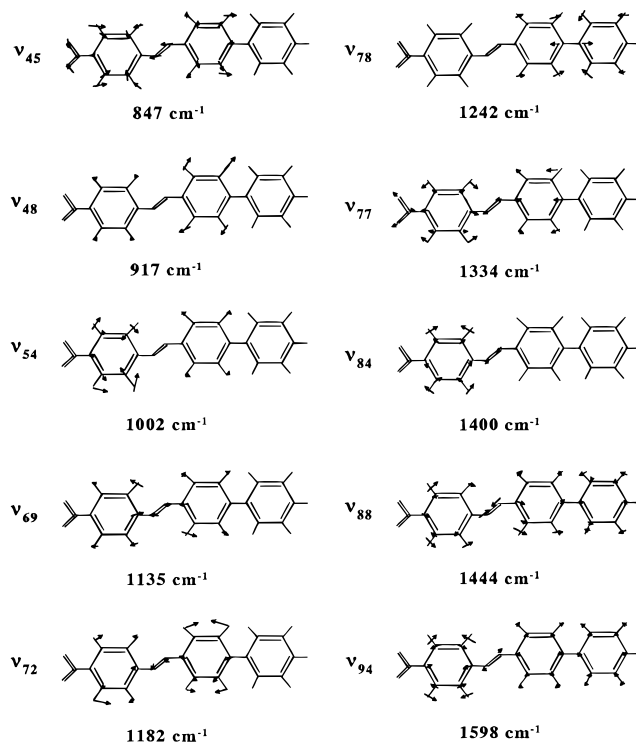
Figure 5. Normal modes calculated for PNAB by Cerius[2] Gaussian routine and their assignments. Nitro group is on the left in all cases. The intensities of the vibrational modes are indicated by the intensities of the arrows. ν_{84} and ν_{88} assignments are uncertain, due to possible errors in the Cerius calculation (see text).

AB and NAB exhibit three bands in the 1400−1500 cm⁻¹ region which have been associated with the N=N group in the literature. Assignment of these three bands to particular modes is somewhat speculative, but we do observe that all three appear to shift to lower energy upon chemisorption. Cerius[2] permits visualization of the normal modes associated with each frequency, as illustrated in Figure 5 for PNAB and listed in Tables 1 and 2.

Bands in the region of 1240−1280 cm⁻¹ (ν_{78}) are quite important, due to their association with the C−C bond between the carbon surface and the adsorbate. For both AB and NAB, this band was apparent for the chemisorbed molecule but not the pure solid. To confirm the assignment as the surface C−C stretch, [¹³C]graphite was substituted for GC and derivatized with natural abundance (i.e., ¹²C) AB. The [¹³C]graphite was purchased as such and then heat treated to 1700 °C for 6 h in vacuum to improve microscopic order and remove impurities. The ¹³C-modified powder was pressed with KBr (20% C/KBr by weight) and then derivatized in CH₃CN with the same procedure as that for GC. Figure 6 shows the 1150−1350 cm⁻¹ range for chemisorbed azobenzene on [¹²C]- and [¹³C]graphite powder. Three different surfaces were derivatized for each case to minimize random error. Most of the observed bands, including those outside of the 1150−1350 cm⁻¹ region, are insensitive to isotopic substitution, but definite changes are observed in the 1246 and 1279 cm⁻¹ bands. The maximum predicted isotope shift is −50 cm⁻¹, which is likely to be quite lower due to the stiffness of the graphite lattice. As shown in Table 2, the Cerius[2] calculation predicts an isotope shift from 1241 to 1224 cm⁻¹ for this mode in 4-phenylazobenzene, with much smaller shifts predicted for other modes which do not involve the C−C linkage. It is not known why bands at 1246 and 1278 cm⁻¹ were observed for AB on [¹²C]graphite, while only one
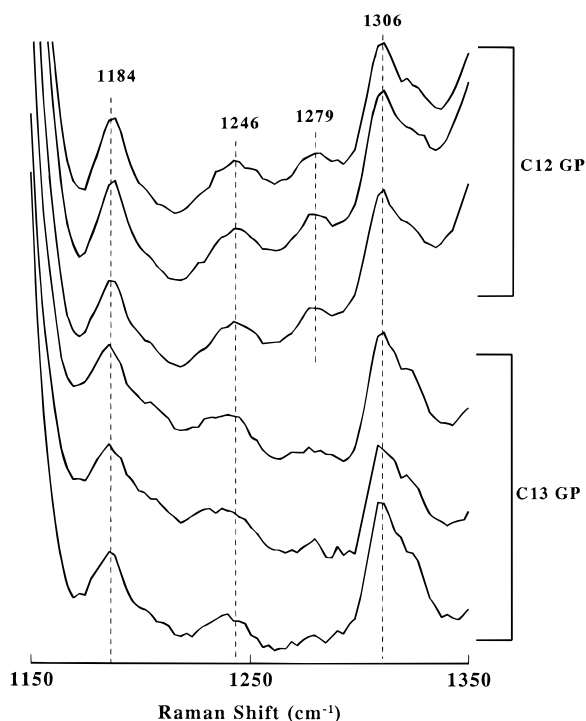
Figure 6. Raman spectra of 1150–1350 cm^{-1} region of azobenzene chemisorbed on [^{12}C]- and [^{13}C]graphite powder pressed in KBr. Each replicate is from a separate sample and derivatization procedure. Integration time in all cases was 30 min, and the underivatized carbon spectra were subtracted.

band was predicted by Cerius^2 for the model compound. Chemisorbed NAB exhibited one band at 1242 cm^{-1} in this region, which disappeared upon ^{13}C substitution in the graphite. The two bands could be caused by different binding sites on the carbon surface.

Although a detailed interpretation of changes in Raman intensities upon chemisorption would require substantially more data than presently available, there are some observations of value. The NO$_2$ stretch relative intensity in NAB decreases significantly upon chemisorption. We noted earlier that Raman cross sections for all bands increase significantly upon chemisorption, but this effect is apparently smaller for the NO$_2$ stretch. A possible explanation is that the azobenzene chromophore is coupled to the graphite ring system, thus increasing its resonance enhancement, while the NO$_2$ group is coupled less strongly. There are also significant relative intensity changes in the 1400−1500 cm^{-1} (N=N stretch region) for NAB, which may also involve electronic interactions between NAB and the graphitic π system.

Depolarization Ratios and Adsorbate Orientation. We have reported previously that Raman depolarization ratios can be useful for deducing absorbate orientation,[14] since adsorbates will not generally be randomly oriented relative to the surface. Partial orientation changes the observed polarization ratio for surface-bound molecules compared to their solution counterparts, often dramatically. Using the experimental procedure described previously, depolarization ratios for chemisorbed DNPH and NAB were determined on GC and the basal and edge faces of HOPG. The notation *a*||*Y* indicates that the graphite *a*-axis (in the graphitic plane) is parallel to the incident electric field vector. For GC, the graphitic axes are random relative to the laser (and surface), so the *a*||*Y* designation is not meaningful. For the case of edge plane HOPG, two polarization orientations are shown in Figure 7. For a given experiment, the carbon sample was oriented relative to the incident laser, and then the 180° backscattered depolarization ratio (ρ_Z) was determined. For GC, the laser was always incident normally on the surface.

Figure 8 shows Raman spectra for DNPH chemisorbed on HOPG edge plane (Figure 8A,B) and GC (Figure 8C). When the **E** field vector is parallel to the graphitic plane (*a*||*Y*) for HOPG, all bands are strongly polarized, with the numerical values listed in Table 3. The spectrum in Figure 8B, for the case where **E**$_Y$
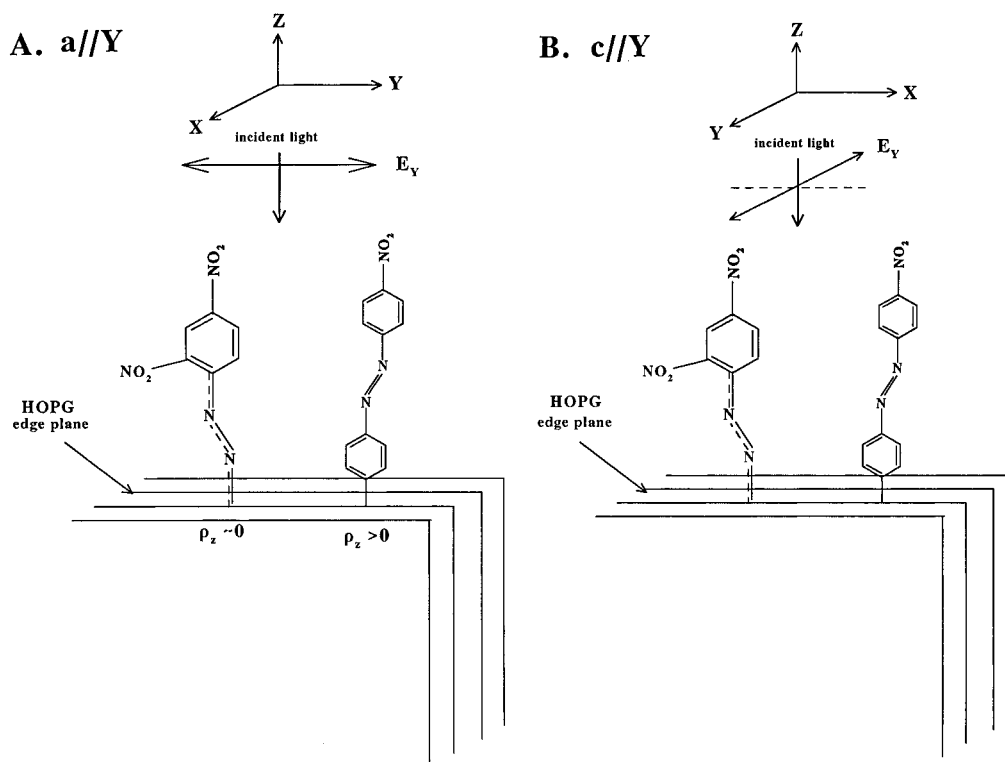

Figure 7. Schematics showing the *a*||*Y* and *c*||*Y* observation geometries, in which the incident electric field vector is parallel or perpendicular to the graphite planes, respectively.
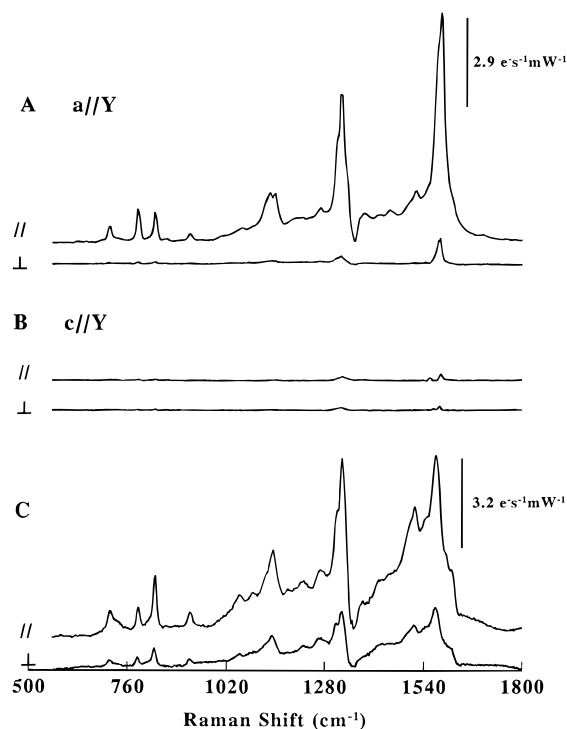
Figure 8. Raman spectra obtained with the indicated polarizations for DNPH chemisorbed to HOPG edge plane. Spectra A and B are on the same intensity scale, and the only difference between the two was a 90° rotation of the graphite crystal about the Z axis of the laser. Spectrum C shows two polarizations for DNPH chemisorbed on GC 20. Laser power was 50 mW, integration time was 15 min.

was perpendicular to the graphitic plane ($d||Y$), is plotted on the same intensity scale as that in Figure 8A and demonstrates that the Raman scattering is much weaker for both polarizations. Both the low ρ_Z for $a||Y$ and the low intensities for $d||Y$ imply that the chemisorbed DNPH is, indeed, oriented parallel to the graphitic planes and that the induced polarization and resulting scattering are quite weak for the $d||Y$ geometry. Figure 8C shows the results for DNPH on GC, with quite different behavior. Since the graphitic planes in GC are not oriented relative to the surface, $\mathbf{E}_Y$ is always randomly oriented relative to the graphitic regions. Polarization ratios are in the range 0.23−0.79, all greater than the largest value observed for HOPG edge plane (0.10). These observations indicate that the chemisorbed DNPH is much more randomly oriented relative to the laser polarization on GC than on HOPG edge. The depolarization ratios for NAB on both GC and HOPG edge (shown in Figure 9 and Table 3) indicate little or no preferential orientation of NAB relative to the graphite plane orientation. The intensities are similar for the $a||Y$ and $d||Y$ orientations, and the depolarization ratios are in the range 0.23−0.45. When NAB was chemisorbed to basal plane HOPG and the laser was incident normal to the basal surface, the depolarization ratios were similar to those observed on HOPG edge or GC, with values ranging from 0.18 to 0.65 (Table 3).

It should be noted at this point that the deductions about molecular orientation ignore differences in mode symmetry which normally affect depolarization ratios. Furthermore, both chemisorbed DNPH and NAB are in partial resonance, thus accounting for their fairly intense surface spectra. It is apparent that the dominant factor determining ρ_Z is the orientation of $\mathbf{E}_Y$ and the molecular plane. The polarizability of both DNPH and NAB will be larger when $\mathbf{E}_Y$ is in the plane of the molecule, and this effect

Table 3. Backscattered Depolarization Ratios (ρ_Z) for Adsorbates on HOPG and GC

DNPH Modified

obsd Raman frequency (cm^{-1})	ρ_Z	
	edge HOPG ($a||Y$)	glassy carbon
715	0.04	0.28
788	0.05	0.39
832	0.06	0.37
924	0.08	0.30
1053	<0.01	0.23
1091	<0.01	<0.30
1141	0.07	0.39
1268	0.09	0.79
1328	0.07	0.32
1516	0.06	0.26
1574	0.10	0.33

NAB Modified

obsd Raman frequency (cm^{-1})	ρ_Z		
	edge HOPG ($a||Y$)	basal HOPG ($c\perp Y$)[a]	glassy carbon
847	0.38	*b*	0.49
917	0.34	*b*	0.26
1002	0.35	0.18	0.31
1135	0.32	0.28	0.27
1182	0.23	0.26	0.28
1242		*b*	
1334	0.25	0.28	0.18
1400	0.32	0.25	0.23
1444	0.38	0.29	0.29
1598	0.45	0.65	0.25

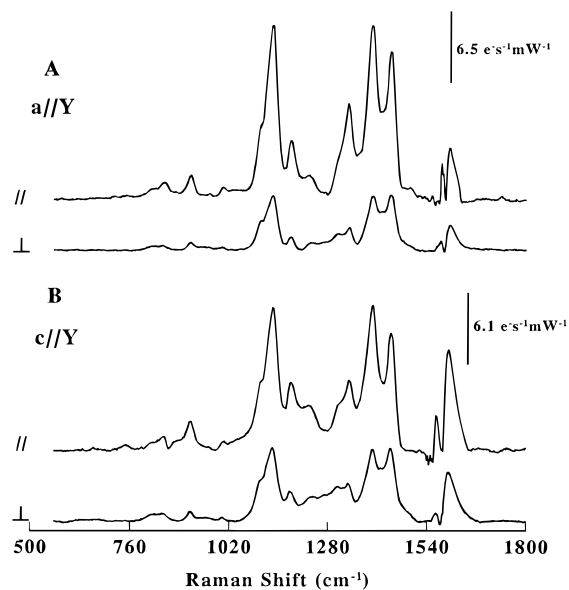[a] For basal plane, $\mathbf{E}_Y$ was perpendicular to graphite *c*-axis. [b] Too weak to determine.

Figure 9. Raman spectra for NAB on HOPG edge, viewed normal to the edge face. Laser power was 50 mW, integration time was 10 min.

may be amplified for preresonant conditions. Furthermore, most of the observed modes are resonance enhanced and, thus, coupled to the delocalized, planar electron distribution in the chromophore of both molecules. Thus, the observed intensities are expected to be strongly dependent on the orientation of $\mathbf{E}_Y$, apparently more so than on mode symmetry. Whatever the origin of the significant differences between ρ_Z on GC or HOPG, these differences allow
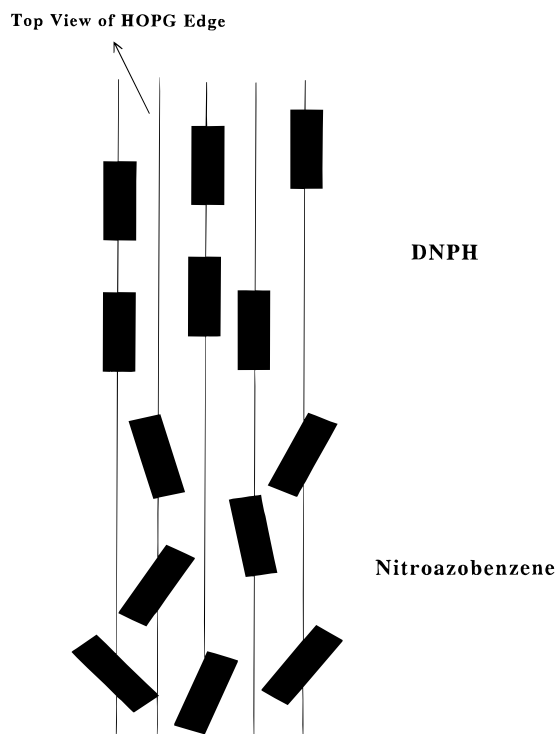
Figure 10. Schematic view of the HOPG edge, viewed normal to the edge face. Rectangles represent chemisorbed DNPH or NAB along the edge, either oriented with respect to the edge (DNPH) or rotating (NAB).

deductions about the effects of the carbon substrate on the orientation of the adsorbate relative to the laser polarization.

We concluded previously that the DNPH adduct to surface carbonyl groups (shown in Figure 7) contains delocalized electrons in the C−N−N−C linkage and some multiple bond character. The polarization measurements imply that this linkage results in restricted rotation along the C−N−N−C linkage and

keeps the nitrophenyl ring parallel to the graphitic plane. This orients the DNPH adduct plane relative to the laser polarization and leads to a ρ_Z close to zero. This geometry probably still occurs locally on GC, but the random orientation of graphitic regions in GC causes depolarization and nonzero ρ_Z. For NAB, the bond between the azobenzene chromophore and graphite plane is a single bond, permitting rotation and much weaker (if any) alignment of the molecular plane with the graphite plane. In addition, rotation about the phenylazo bonds may occur, further randomizing the orientation of the molecular plane relative to $\mathbf{E}_Y$. Thus, the substrate has little effect on observed polarization, even if the substrate itself is oriented relative to $\mathbf{E}_Y$. This situation is shown schematically in Figure 10 for a view along the axis normal to the HOPG edge. The rectangles represent chemisorbed DNPH and NAB molecules. Although it would be surprising if the NAB molecules can rotate freely on HOPG edge, given likely steric hindrance from adjacent molecules or graphite planes, the polarization ratios imply much more rotation than that allowed for DNPH. On HOPG basal plane, the NAB molecules are rotationally disordered relative to $\mathbf{E}_Y$. There may be microscopic domains where the NAB molecules preferentially orient relative to one other, but these domains must be small compared to the area sampled by the spectrometer.