Structural Analysis of Char by Raman Spectroscopy: Improving Band Assignments through First Principle Computational Calculations

Matthew W. Smith^{1,4}, Ian Dallmeyer², Timothy J. Johnson³, Carolyn S. Brauer³, Jean-Sabin McEwen^{4*}, Juan F. Espinal⁵ Manuel Garcia-Perez^{1*}

¹*Department of Biological Systems Engineering, Washington State University, Pullman, WA 99164, USA*

²*Composite Materials & Engineering Center, Washington State University, Pullman, WA 99164-2262, USA*

³*Chemical Physics & Analysis, Pacific Northwest National Laboratory, Richland, WA 99352, USA*

⁴*Gene and Linda Voiland School of Chemical Engineering and Bioengineering, Pullman, WA 99164, USA*

⁵*Chemistry of Energy Resources and the Environment, Insitute of Chemistry, University of Antioquia, Medellin A.A. 1226, Colombia*

(Paper submitted to Carbon)

**Corresponding authors:*

Manuel Garcia-Perez	Jean-Sabin McEwen
Associate Professor	Assistant Professor
Department of Biological Systems Eng.	Voiland School of Chem. Eng. and Bioengineering.
LJ Smith, Room 205, PO Box 646120	Wegner 257, PO Box 646515
Pullman, WA 99164-6120	Pullman, WA 99164-6515
Phone: 509-335-7758	Phone: 509-335-8580
e-mail: mgarcia-perez@wsu.edu	e-mail: j.s.mcwen@wsu.edu

Abstract: The complex heterogeneous nature of chars has confounded the complete analysis of the Raman spectra of these materials. The additional shoulders observed on the defect (D)-band and high intensity valley between the D and graphitic (G)-bands represent the primary regions of uncertainty. In this paper the effects of various vacancy and substitution defects in a coronene parent molecule have been systematically analyzed using density functional theory (DFT). The impacts of these defects are best understood in terms of a reduced symmetry as compared to a “parent” coronene molecule. Based on simulation results, a total of ten potential bands have been assigned between 1000 cm^{-1} and 1800 cm^{-1} . These bands have been used to deconvolute a thermoseries of cellulose chars produced by pyrolysis at $300\text{-}700\text{ }^{\circ}\text{C}$. The shoulder observed in chars near 1200 cm^{-1} has been assigned to the symmetric breathing mode of various small polycyclic aromatic hydrocarbons (PAH) as well as rings containing seven or more carbons. Intensity between 1400 cm^{-1} and 1550 cm^{-1} results from a range of coupled vibrational modes from various defect structures. The deconvolution of cellulose derived chars shows consistent growth of PAH clusters, loss of oxygen, and development of non-hexagonal ring systems as pyrolysis temperature increased.

1. Introduction

Carbonaceous materials from biomass have been studied for a vast array of applications, with use in activated carbon production or as reducing agents in metallurgical applications are the most common [1, 2]. Application of biomass-derived chars to environmental applications has also gained support in the last decade [3]; this interest stems largely from applications in carbon sequestration [4-7], soil fertility [8, 9], and water treatment [10, 11]. In addition, the electrical properties of carbons produced at higher temperatures have spurred the investigation of their use in super capacitors [12], and metal ion batteries [13-15]. Despite the wide range of applications for amorphous, non-graphitizing, carbons, the highly heterogeneous nature of these materials can lead to significant challenges in characterization by spectroscopic techniques such as Raman scattering [16-18].

Non-graphitizing carbons have historically been modeled as small, randomly oriented graphene-like sheets (see Figure 1A) [19]. Such models have been employed in nuclear magnetic resonance (NMR) studies to identify overall cluster sizes for chars produced at low temperature, determining clusters to be small, approximately 8-27 rings for chars derived from pyrolysis and gasification [20, 21]. Despite the tendency to model biochars as simple systems, a complex structure is known to exist. These structures result from the degradation of heterogeneous lignocellulosic materials by an array of solid-gas, solid-liquid and solid phase thermochemical reactions [22-27]. More specifically, NMR studies of biomass pyrolysis chars have identified aliphatic fractions in pyrolysis chars, and to a lesser extent gasification chars [20, 21]. High resolution imaging techniques have highlighted the warped nature of carbon clusters in activated carbons, and the inclusion of non-hexagonal ring systems in the structure of these materials [28, 29]. Figure 1B shows a schematic representation of the curvature identified in activated carbon regions by Harris et al. [28]. In addition, several oxygenated groups are known to be stable at temperatures between 300 °C and 700 °C [30, 31] and add to the complexity of the structure. Figure 1B shows a fullerene-like sheet, proposed by Harris et al. [25] as the basis for structures in activated carbon. Figure 1C shows the collapsed 2D model of coal proposed by Shinn [32] which depicts the complexity of oxygenated groups and defects within the carbon matrix.

Several simulations have also been carried out using a variety of computational packages to generate 3D representations of coal [33] and nano-porous carbons [34].

Analytical methods for the study of chars and activated carbons by Raman spectroscopy are typically based on graphitic structures and can be traced to the seminal work of Tuinstra and Koenig [35] in 1970. The authors identified the graphitic G-band, located at approximately 1575 cm^{-1} , as the primary Raman active mode for highly ordered regions of graphite crystals. A second distinct mode, the D-band, near 1350 cm^{-1} , was resolved by the authors when defective regions near grain boundaries were analyzed [35]. Further work by Vidano et al. [36] in 1981 determined that the position and intensity of this peak is dependent on the excitation wavelength. This behavior was linked by Thomsen and Reich [37] in 2000 to a double resonance process. Excellent reviews of fundamental Raman active modes of graphitic systems have been completed by Thomsen and Reich [38] and Pimenta et al. [39]. Ferrari and Robertson [40] also reviewed the application of Raman to amorphous and diamond like carbon. In the last decade, significant work has been completed on the characterization of graphene by Raman spectroscopy as reviewed by Ferrari and Basko [41].

The physical description of the origins of the D and G-bands have been a vital guide to understanding the deconvolution and interpretation of graphite-like carbons [38]. While the same deconvolution and analysis methods used for graphite have been applied to amorphous carbons, analysis of the D and G peak is not sufficient to capture the full complexity of the systems [16, 17, 40, 42, 43]. Deconvolution of spectra from char and activated carbon systems often utilizes several additional peaks to improve the fit of shoulders not typically represented in spectra from graphitic materials. These bands have not yet been definitively assigned [16, 43]. Figure 2 shows the application of three deconvolution methods reported in the literature to the Raman spectrum of a cellulose pyrolysis char produced at $400\text{ }^{\circ}\text{C}$ for this study. While several other methods have been reported [16, 44, 45], these methods demonstrate the varying complexity of models that have been employed in the deconvolution of Raman spectra for a variety of carbon systems.

Figure 2A shows the simplest deconvolution as described by Ferrari et al. [40, 42]. This method uses two curves to fit data, a broad Gaussian to fit the primary D-band and an asymmetric Briet-

Wigner-Fano (BWF) peak is used to represent the G-band. This method is excellent for analysis of well-ordered systems such as graphite, but fails to accurately reproduce the complexity of the cellulose char spectrum. Figure 2B depicts the deconvolution method employed by Hu et al. [43]. This method partially addresses the complex nature of the curve by inclusion of a transpolyacetylene (TPA) peak near 1200 cm^{-1} , and an amorphous region (A-band) near 1500 cm^{-1} . The TPA, D and A bands are each modeled using Gaussian type curves while the G-band is modeled using a Lorentzian peak. A final Gaussian peak located approximately 30 cm^{-1} higher than the G band is added to capture a double resonance breathing mode described by Thomsen and Reich [37, 38]. While this method improves the fit with the experimental spectrum, it still does not demonstrate adequate complexity to fit the low wavenumber region. Moreover, uncertainty remains in the assignment of both the TPA and A bands. Figure 2C shows the deconvolution method employed by Li et al. [17]. In this method four regions are utilized to characterize the material, these include: the shoulder (S), defect (D), valley (V) and graphitic (G) regions. These regions are further subdivided into a total of 9 peaks, represented by: S_R , S , S_L , D , V_R , V_L , G_R , G , and G_L , where L and R subscripts denote left and right respectively. It must be noted that this method was designed for use with Raman spectra collected at 1064 nm : However because the D-band is dispersive with energy, the peak labels shown in Figure 2C are not accurate. The D-band should be red shifted by approximately 50 cm^{-1} to compensate for variance in the excitation energy of the incident light used [36]. However, the red shift required for the V_R and V_L bands is unknown. Despite errors in labeling when applied to a spectra collected at 532 nm , this method provides an exceptional fit to the experimental data, however the peak assignments provided are based on results limited by the availability of model surrogate compounds for many of the char structures, leaving uncertainty in the assignments.

To better identify potential compounds responsible for spectral intensities in the S and V regions discussed by Li et. al. [17] (or TPA and A as presented by Hu et. al. [43]), spectra from a range of disordered carbons structures are required. Here recent advances in computational chemistry can allow for the rapid screening of the Raman spectra of an array of structures that would otherwise be difficult or impossible to isolate [46]. Molecular dynamic simulations have already been employed for several model compounds to determine the origins of various vibrational modes, and have demonstrated the capacity of DFT based models to accurately reproduce the

experimental spectra of a range small carbon compounds [47], small polycyclic aromatic hydrocarbons (PAH) [48], and modified graphene and graphite [49]. Simpler computational methods have also been applied to large PAHs [50, 51].

In this paper both experimental and calculated Raman spectra from small PAH molecules are used to assist in the deconvolution of Raman spectra from complex carbonaceous materials derived from lingo-cellulosic feedstock processed at low temperatures. The molecules studied were chosen to represent the effects of cluster size, non-hexagonal systems, point defects, alkene groups, and heteroatom substitutions. The new deconvolution method is then used to evaluate the structural evolution of chars produced from Avicel cellulose. Avicel cellulose was chosen to provide a reasonably consistent and widely available initial feedstock, and is expected to produce many of the same spectral features as native biomass after pyrolysis.

2. Materials and Methods

2.1 Model compounds

All model compounds were purchased from Sigma Aldrich with a minimum purity of 95% and used as received, these standards include: naphthalene (product# 184500), pyrene (product# 572145), perylene (product# P1104), benzo[a]pyrene (product# B1760), benzo[g,h,i]perylene (product# B9009), coronene (product# C84801), and anhydrous tetracarboxylic perylene (product# P11255). All samples, except naphthalene, were mixed at a rate of 5 wt % with spectroscopic grade KBr (LOT# BCBD3066V) prior to analysis. Naphthalene, due to its high crystallinity and comparatively low Raman intensities was analyzed neat. KBr mixtures were employed to ease material handling during packing and to minimize any potential heating effects [17].

2.2 Cellulose pyrolysis chars

A series of five chars was produced from avicel cellulose (LOT# BCBG9043V) at final heating temperatures between 400 °C and 700 °C using a spoon pyrolysis reactor following the method

described by Wang et al. [26]. Briefly, the reactor was preheated to the desired temperature and the sample placed in a water-jacketed cooling zone prior to the furnace. The chamber was purged with N₂ gas (99%) at approximately 300 mL/min for a minimum of 10 minutes prior to treatment. At the start of the experiment the sample was introduced into the furnace and allowed to react for 30 minutes before withdrawal to the cooling zone. A secondary preheated nitrogen sweep gas, of approximately 550 mL/min was employed in the reactor zone to minimize vapor-char interactions. Samples were allowed to cool to temperatures below 25 °C before exposure to air. Sample temperature was monitored continuously by three exposed type-k thermocouples placed within the sample using an ExTech SDL200 temperature meter.

2.3 Experimental FT-Raman methods

1064 FT system: To avoid potential fluorescence, all model compounds were analyzed by collecting Fourier transform Raman spectra with an FT-Raman spectrometer using 1064 nm excitation and 4 cm⁻¹ resolution. The FTIR-Raman instrument and parameters have been previously described [52, 53]. A Bruker IFS 66v/S spectrometer with a FRA 106 Raman accessory employing a CW Nd:YAG laser was used. The laser has a nominal line at 9397.58 cm⁻¹ (air) absolute frequency, but can have daily variations of ± 0.50 cm⁻¹ [53, 54]. The FRA 106 accessory allows either focused or unfocused laser spot with either 90° - or 180° backscatter light collection. Samples were pressed into standard aluminum discs, and the unfocused mode was used to collect the 180°-backscattered light.

Calibration was performed for both the scattered light recording system and the frequency of the Raman excitation laser. To calibrate the interferometer HeNe laser frequency we use a series of five Hg lines known to span the spectral range of interest; these were compared to known NIST (air) values, and the HeNe frequency adjusted such that the mean deviation for all five lines is ≤ 0.2 cm⁻¹. The absolute wavelength of the Raman excitation laser was then calibrated using the equivalence of the Stokes and anti-Stokes frequency shifts; the Raman Nd:YAG 1064-nm laser wavenumber is set using the Stokes/anti-Stokes bands from a sulfur standard with Raman bands at ±479 cm⁻¹. The excitation frequency was adjusted until the agreement was within

$\pm 0.20 \text{ cm}^{-1}$, which is significantly smaller than the inherent Raman laser linewidths of room temperature solid samples. The measured spectra were also corrected for the intensity response of the system [54]. Laser powers of 100 and 300 mW were used to collect spectra from naphthalene and a laser power of 100 mW was used for all other standards. All spectra presented are the average of 100 interferograms. Data were transformed with power phase correction to deliver spectra in the range of $+3,600$ to $+100 \text{ cm}^{-1}$ Stokes shift and ca. -100 to $-1,100 \text{ cm}^{-1}$ anti-Stokes shift.

532 system: Dispersive Raman spectra were collected for all standards as well as each cellulose pyrolysis char samples using a Horiba LabRAM HR microscope. A 250-mW, 532-nm wavelength laser (Ventus LP 532) operated at 90% of maximum intensity with a 1% transmittance filter was used for visible light analysis at an objective of 50x. The spot size is estimated as an ellipse with a major axis of $25 \mu\text{m}$ and minor axis of $20 \mu\text{m}$ for the visible laser, resulting in an average power of 229 W/cm^2 applied to the surface. Duplicate analysis of the initial spot was performed after a five minute cooling period to ensure a consistent signal was obtained. Spectra were collected from a minimum of three separate points on each sample with four scans per replicate.

Sharp background peaks were noted for all samples collected on the 532 nm system; these peaks were removed in post processing using a blank scan and the resulting primary peak at 2437 nm as the reference. After correction all spectra were normalized using the maximum intensity of the G-band near 1600 cm^{-1} as the reference. A boxcar average over 7.5 cm^{-1} was employed to smooth the final curve. To increase the signal to noise ratio, the corrected spectra from each replicate were then averaged to create a final composite curve for peak analysis.

2.4 Computational methods

A series of PAHs were studied to confirm the validity of simulation results against experimental spectra. Simulations were conducted on a range of defective structures based on an initial coronene system. Coronene was selected as the basis for defect studies as it represents the smallest PAH in which single and double point defects can be easily introduced. After

constructing and optimizing a coronene system, one or two carbon atoms were removed from the center to create the defect. The system was then brought back to a charge neutral structure through formation of 5-membered rings and/or hydrogen additions to create a series of possible point defects. Oxygen and nitrogen substitutions were also used to create defective structures and tests the effects of heteroatom substitution. A series of systems containing oxygenated edge sites were analyzed to determine the effects of recalcitrant oxygen fractions as well as the possible impact of post treatment oxidation, which is known to rapidly alter edge sites upon air exposure [55]. An alkene modified coronene system was studied to examine the potential impact of TPA type compounds on the spectra near 1200 cm^{-1} [43]. Cyclopentane and cycloheptane based ring systems were examined to isolate the impact of non-hexagonal rings on the final Raman spectra based on the suspected origins of intensity between the D and G-bands [16, 43].

All compounds have been evaluated using most abundant isotopes in the Gaussian 09 rev. B.01 software package [56]. Geometry optimizations and frequency analyses were completed using the Becke three-parameter Lee-Yang-Parr (B3LYP) hybrid functional [57]. Four basis sets were chosen based on the larger study of Cheesemen et al. [47]. These basis sets include a Pople type split valence 6-31G* basis set [58], a Dunning's correlation consistent polarized valence double zeta basis set (cc-pVDZ) [59] and two of Dunning's augment correlation consistent basis sets (aug-cc-pVDZ and aug-cc-pVQZ) [60]. The simulated spectra at each level were obtained for naphthalene and compared to experimental results. All of the larger systems were evaluated only at the 6-31G* level. Previous investigations using PAHs have demonstrated effective prediction of Raman peak positions with DFT after appropriate scaling [61-63]. Input parameters for each compound studied were constructed using the WebMO platform [64] with a preliminary geometry optimization. For each compound, the singlet state multiplicity was confirmed by comparing the energy of the optimized singlet and triplet states. Following optimization of the geometry and force constants at the desired theory level, frequency calculations were performed at the static limit. Raman spectra and vibrational modes are visualized using the WebMO tool [64]. All simulated spectra are visualized using a Lorentzian peak shape with a full width at half maximum (FWHM) of 4 cm^{-1} for each vibrational mode. For comparison, all spectra were normalized based on the peak of maximum intensity between 1000 and 1800 cm^{-1} .

2.5 Deconvolution of Dispersive Raman Spectra from Cellulose Char

All spectra were analyzed between 900 cm^{-1} and 2000 cm^{-1} . A linear background correction was employed using the minimum intensity between 900 to 1000 cm^{-1} and 1800 to 2200 cm^{-1} as anchor points. These regions bracket the initial and final regions where clear signals from the char spectra are obtained.

Deconvolution of the Raman spectra was conducted using the peak fit pro tool in the OriginPro 2015 software package (OriginLab, Northampton, MA). All peaks included in this method utilize a Gaussian profile, except the G_L peak which is specified with a Lorentzian profile. Detailed discussion of each peak is provided in section 3.5. In this procedure the D and G_L peaks are set based on the local maxima near 1350 and 1600 cm^{-1} , respectively. Peak parameters were initially estimated, with all others fixed near 0 intensity and run for 200 iterations to obtain a reasonable fit. The remaining peaks were then centered based on shoulder locations and the intensities were allowed to vary. The FWHM values were also allowed to vary from 50 - 100 cm^{-1} in this step. Curve fitting was allowed to progress for 20,000 iterations or until tolerance of 1×10^{-6} achieved. Finally, all peak positions were unlocked and the system allowed to converge until a tolerance of 10^{-9} was achieved. After convergence, if the FWHM of any peak reached 100, the bound was increased to 120 and rerun to allow accurate fits. The method described above was utilized to avoid excessive peak drift or broadening during fitting. However, it should be noted that, due to the complexity of the spectra and the number of peaks utilized, truly unique fits do not exist. Modification of the peak parameters or fitting procedure can result in substantial variance in the deconvolution which will alter interpretation of the results.

3. Results and Discussions

3.1 Selection of basis sets for calculations

The effect of basis sets on the accuracy of the calculated Raman spectra for naphthalene was evaluated by comparing the simulated spectra from several different basis sets to the

experimental spectra as shown in Figure 3. Each basis set was largely capable of reproducing the primary vibrational modes observed in the experimental results, though variations in predicted peak intensity were observed. Errors in position are largely a result of the B3LYP functional utilized for all calculations [62]. Peak intensity errors were calculated based on the normalized root mean square error of intensities for all peaks with intensities greater than 0.05. The hydrogen stretching modes above 3000 cm^{-1} were excluded as these modes are most sensitive to the phase variance between experimental (solid) and simulated (gas) spectra. Each major peak position and the related intensity are reported in Table 1. Also included in are the %NRMS error in position and intensity for each basis set.

The results shown in Figure 3 and Table 1 indicate good prediction of the vibrational frequencies for each basis set chosen, but the most accurate frequencies were predicted by the augmented basis sets. The 6-31G* basis set was the lowest theory level utilized and required the least CPU time to analyze. Despite this, the most accurate intensities were obtained from this method. The 6-31G* basis set was capable of capturing all major and minor observed vibrational modes with only minimal loss of accuracy, and without specifying significant additional signals, this basis set was deemed acceptable for the purpose of identifying distinctive regions for curve deconvolution. All further simulations were carried using this simple basis set.

Errors in peak position for simulated spectra were evaluated by comparison with experimental peaks for naphthalene, pyrene, perylene, benzo[a]pyrene, benzo[g,h,i]perylene, and coronene. Offsets were found to have a generally linear characteristic with calculated peak position, though some deviation was observed at both the low and high wavenumbers. For the frequency range of interest, between 1000 and 2000 cm^{-1} a single parameter linear correction factor of 0.9726 [63] accounted for the great majority of calculation error when using the 6-31G* basis set.

3.2 Effect of cluster size and symmetry on Raman signal

In terms of Raman band intensities for different aromatic species, the relative intensity of the most prominent peak for each compound is summarized in Table 2. It is noted that despite the use of pure naphthalene in the experimental analysis, the peak intensities remained considerably

lower than for any of the other PAH study, all of which represent spectra obtained from 5 wt % dilutions in KBr. This result follows a trend highlighted by Li et al. [17] which shows only very low concentrations of sample in a KBr solution, less than 2% for char, are required to achieve 100% signal [17]. While the predicted relative intensities are considerably lower than experimental results for both pyrene and benzo[g,h,i]perylene and higher for coronene, calculated intensities are reasonably accurate for perylene, and benzo[a]pyrene. Despite the strong discrepancies in overall intensities, the relative peak profiles within each simulated spectrum closely followed the experimental profile. The differences observed are likely linked to resonant enhancement of various vibrational modes which will be a focus of future work.

Comparison of the experimental and simulated Raman spectra for each PAH is presented in Figure 4. Simulated results (solid lines) have been frequency-corrected based on the single parameter factor given by Hall et al. [63]. All spectra are represented based on relative intensity compared to the most prominent peak between 600 cm^{-1} and 2000 cm^{-1} for each spectrum. After correction, frequencies obtained from DFT simulation show good agreement with the experimental results (dashed lines) within this range. While the simulated results generally fit very well with the experimental data, an important deviation is noted for coronene: a doublet peak structure is present near 1380 cm^{-1} in the experimental spectra, while only a singlet is identified in the simulation. This effect may be due to mild asymmetry in the solid-phase sample distorting the idealized D_{6h} symmetry used in the gas-phase model. Three primary vibrations are identified within each PAH, with the location of the primary peaks marked by black lines overlaid on figure 4A. These modes consist of symmetric, or asymmetric breathing modes, Kekulé vibrations, and asymmetric stretching. Each of these modes is visualized in figures 4B-4D respectively for a simple benzene system, though it must be stated that the symmetry will differ and these modes only represent approximate motion. Several peaks within each spectra also develop as a result of mixing of these primary modes.

A spectrum collected from benzo[g,h,i]perylene using the 532 nm system previously described was compared to the spectrum collected using the 1064 nm system (data not shown). Though the signal to noise decreases dramatically due to fluorescence, all major peaks were found to agree to within 1 cm^{-1} . Because the D-band of larger aromatic systems such as activated carbon and

graphite is known to be dispersive with **excitation energy**, confirming that the larger ring systems do not show dispersive behavior was necessary before applying these results to the analysis of spectra collected under different excitation wavelengths.

Table 3 lists the positions, intensities and origins of the most important vibrational modes seen in Figure 4. The **frequencies** of the simulated **modes** have again been corrected using a correction factor of 0.9726. From these results two primary modes are clearly observed between 1000 cm^{-1} and 1410 cm^{-1} ; the first is the totally symmetric ring breathing A_{1g} mode, depicted in Figure 4b, which appears at 992 cm^{-1} for benzene [54] at 1000 cm^{-1} for naphthalene and increases logarithmically with cluster size to 1350 cm^{-1} (shown as a black line in Figure 4). The second mode is that of Kekulé vibrations for each compound. The position of this mode varies inconsistently in position for each compound but is typically located between 1360 cm^{-1} and 1410 cm^{-1} . The only exception to this is coronene where, due to a high degree of symmetry, these modes have collapsed into a single normal mode containing both the A_{1g} breathing mode **by the** center ring and the Kekulé type vibrations in the **outer** rings. The split modes observed in the experimental spectrum of coronene, however, suggest that the solid phase does not fully retain the idealized D_{6h} symmetry of the gas-phase prediction, giving rise to two slightly shifted modes. An assortment of larger ring structures, studied by Negri et al. [50], show a similar trend of combined A_{1g} and Kekulé type vibrations. These modes, concentrated between 1350 cm^{-1} and 1250 cm^{-1} , **often give** rise to two distinct peaks within this region. A third peak can also be resolved depending on the structure of the PAH, presenting as a shoulder on the peak nearest 1350 cm^{-1} .

The effect of not only cluster size, but symmetry, becomes apparent when examining the spectra of benzo[a]pyrene and benzo[g,h,i]perylene. Naphthalene, pyrene, and perylene each belong to the D_{2h} point group and show distinct splitting of the symmetric breathing and Kekulé vibrational modes. Reducing the symmetry to C_{2v} , as seen for benzo[g,h,i]perylene, results in the formation of two doublet sets near the symmetric breathing and Kekulé modes of perylene. As expected, lowering the symmetry to C_s , as seen in benzo[a]pyrene, shows still further splitting of the vibrational modes, with the Kekulé type vibrations near 1400 cm^{-1} becoming the most intense. The G-band region shows similar peak splitting as the D-band region, though the position shifts

are less pronounced. The observed peak splitting in the G-band is narrow enough to likely be viewed as a broadening factor in highly heterogeneous materials, however distributions of ring breathing and stretching modes in the region of the D-band are sufficient to result in at least two broad peaks even for large polyaromatic systems [50].

The results of this investigation suggest that for solid carbons containing significant quantities of small polycyclic moieties such as pyrene or perylene **the region** near 1370-1410 cm^{-1} would be expected to **broaden** and gain intensity due to Kekulé vibrations. These compounds would also **be expected to** contribute significantly to intensity in the range of 1250-1300 cm^{-1} , where ring breathing modes dominate. High concentrations would be expected to result in relatively well defined peaks, while low concentrations should result in minor shoulders attached to a primary D-band (larger polycyclic clusters).

3.3 Computational study on the effect of defects and strained ring systems

The **introduction** of several defect structures **into the PAH model systems results** in a strong degradation of symmetry relative to either the benzene or coronene “parent”. This loss of symmetry **lifts** the degeneracies associated with certain irreducible representations of the D_{6h} point group, and **results in** several formerly Raman-forbidden normal modes **becoming** allowed; this has already been seen for many the modes previously discussed for certain hexagonal polyaromatic systems. **The** nature of these vibrational modes **is** largely analogous to the modes present in benzene or coronene and can be interpreted as such. For **simplicity**, the vibrational modes will be presented based on analogous benzene modes, these include: Breathing modes (A_{1g}), Kekulé vibrations, and asymmetric stretches (E_{2g}). In addition, semi-circular breathing modes are also present and become allowed in these much less symmetric ring systems. Because of the generally amorphous structure of char, our analysis **is** limited to **the** evaluation of changes in position and **intensity** of these generalized modes as a **result of structural variations in the** carbon systems.

3.3.1 Computational study on the effect of alkyl side groups

In attempts to deconvolute Raman spectra of activated carbons, several authors have assigned TPA type molecules to a characteristic shoulder often observed between 1150 cm^{-1} and 1200 cm^{-1} [16, 42-44]. To assess the validity of this assignment the Raman spectra of a deca-penta-ene chain was again calculated at the same B3LYP/6-31G* theory level. The resulting frequency-corrected spectrum is depicted in Figure 5. In addition, the spectra of coronene with one and two buta-di-ene side chains were also evaluated. Both the lowered symmetry (C_1 for one chain and C_s for two chains) and the addition of the chains resulted in a split of the parent E_{2g} asymmetric stretch mode near 1600 cm^{-1} , and the development of a second asymmetric mode near 1650 cm^{-1} related to asymmetric stretches in the free side chains. The spectra presented in Figure 5 shows breakdown of the D-band when side chains are added, due in part to a loss of degeneracy but also to mixing of the parent A_{1g} breathing mode with carbon stretch modes within the alkyl chain. No significant peak formations near 1150 cm^{-1} were observed in relation to the buta-di-ene chains. It should be noted that the original assignment by Ferrari and Robertson [65] of the TPA peak was based on evaluation of nano-crystalline diamond produced by chemical vapor deposition. A strong presence of TPA is not expected in chars or other carbons processed at temperatures much higher than $400\text{ }^{\circ}\text{C}$ as the reaction and decomposition of these groups has been reported to become significant at $420\text{ }^{\circ}\text{C}$ [66]. While TPA type groups may contribute to peak intensity near 1150 cm^{-1} , the results suggest that the primary origin of this region is related to different carbon structures.

3.3.2 Isolated effect of non-benzene ring centers

Isolation of a cyclopentane centered ring system (a fragment of a C_{60} fullerene) with a C_5 symmetry shows an intense Raman active band containing mixed breathing and Kekulé type vibrations near 1450 cm^{-1} , as seen in figure 6A. No significant vibrations near the typical D-band are observed despite a strong aromatic character, highlighting some of the difficulty in assignment when non-hexagonal systems are present. A secondary peak, comprised of a mixture of breathing and asymmetric stretch vibrations, is observed as a shoulder near 1470 cm^{-1} . The second important peak near 1600 cm^{-1} is the typical asymmetric stretch common of most sp^2 ordered carbons. These results are highly consistent with published spectra for C_{60} [67, 68].

A cycloheptane centered cluster was also modeled. This system contains only a single mirror plane of symmetry resulting a C_s point group. The overall distribution of Raman active modes is similar to that of benzo[g,h,i]perylene with a C_{2v} grouping. Figure 6B shows the simulated Raman spectrum for the cycloheptane centered system, while the insert highlights the vibrational mode near 1200 cm^{-1} . Vibrations near 1000 cm^{-1} and 1200 cm^{-1} are the result of symmetric breathing modes originating in the cycloheptane center. The most intense band, near 1350 , represents several vibrational modes containing an assortment of strained Kekulé vibrations in the surrounding hexagonal rings mixed with semi-circular breathing of the heptane center. Mixed breathing and asymmetric stretch vibrations are visible near 1500 cm^{-1} . The asymmetric stretch mode is split into three peaks: a weak peak is observed near 1585 consistent with most PAH and graphitic systems, while the two additional peaks are blue shifted towards 1650 cm^{-1} , consistent with spectra from cyclooctane and cycloheptane containing ring systems as presented by Minaeva et al. [69] and Kudin et al. [49] respectively. These peaks contain asymmetric stretches within the hexagonal rings, while the heptane ring demonstrates semicircular and circular breathing modes respectively for the peaks at 1630 and 1660 cm^{-1} .

3.3.3 Effect of single and double point defects

To explore the effect of defective ring structures on the Raman spectra of PAH a variety of defects have been modeled using a coronene ring system as a basis. Coronene was chosen for two reasons: First, previous NMR studies reported in the literature have estimated that compounds of this size are representative of the average molecular structure of char [20, 21], and second because the relatively small size allows for rapid computation of many different configurations. The base system was modified by inclusion of single and double point defects stabilized by (1) creation of strained ring systems such as pentane and octane rings; (2) introduction of hydrogen at defect points; and (3) generation of ether and/or carbonyl groups and (4) nitrogen inclusion in the coronene structure.

Figure 7 shows the computational results of modification of coronene around a single point defect (SPD). These defects greatly reduce the symmetry of the system and show strong alterations of the resulting Raman spectra. The open defect seen in SPD-I results in a C_s

symmetry. Vibrations near 1200 cm^{-1} contain well-formed breathing modes of the intact benzene rings, while the doublet peak near 1370 cm^{-1} is the result of splitting of the parent A_{1g} vibration of coronene. These peaks result from Kekulé vibrations in two pairs of dissimilar benzene rings within the system. In both cases the center of the molecule maintains motion characteristic of a circular breathing mode analogous to unaltered coronene. Both the SPD-II and SPD-III are highly asymmetric, lacking all but the trivial rotational symmetry. The peak near 1450 cm^{-1} seen in SPD-II and SPD-III is a result of the mixed breathing mode of cyclopentane rings and Kekulé vibrations in the surrounding hexane rings shown previously in figure 6A. Low frequency modes between 1100 cm^{-1} and 1200 cm^{-1} develop in the SPD-II spectra due to a combination of in-plane breathing modes of the center defect and hydrogen wags. A range of asymmetric stretch vibrations were available due to the highly asymmetric defect structure, resulting in split peaks within the G-band region near 1600 cm^{-1} . The same trend was also observed in SPD-III; however, the distortion caused by two adjacent cyclopentane rings resulted in the blue shift of these modes to near 1550 cm^{-1} . Inclusion of nitrogen as a point defect (SPD-N) resulted a C_{2v} system containing many of the same peaks as observed in the SPD-I spectra. This is due to similar changes in the overall configuration of the system. In addition a single sharp peak is noted near 1650 cm^{-1} , this peak resulted from strong asymmetric stretches in the two unconstrained nitrogen-containing rings.

Figure 8 shows that the effect of double point defects (DPD) on the Raman spectra of coronene based compounds was even more pronounced than for SPD. Of the defects studied, DPD-II reveals by far the most complex Raman spectrum. This is readily understood in terms of group theory: upon substitution, the coronene D_{6h} point group symmetry is lowered to C_s symmetry in the case of the DPD-I and DPD-III (single mirror plane) systems, and to C_1 symmetry in the case of DPD-II (trivial rotation only). The lowered symmetry and high variability in bonding throughout the system results in many modes splitting and/or becoming Raman allowed. In all cases, a strong relative enhancement of the asymmetric stretch modes are observed when compared to the parent coronene spectrum.

The splitting of the coronene A_{1g} mode between 1300 cm^{-1} and 1400 cm^{-1} observed for DPD-I is analogous to the splitting described for SPD-I. As in the SPD-I spectrum, a peak near 1200 cm^{-1}

is observed, originating from symmetric breathing of the intact benzene rings. The strong peak near 1530 cm^{-1} is the result of mild mixing of asymmetric stretching modes of each carbon with weak semi-circular breathing from the unaltered 3-ring system. The same primary peaks are observed in DPD-III within the $1500\text{-}1600\text{ cm}^{-1}$ region. In contrast, the spectrum for SPD-I did not show any significant mode near 1530 cm^{-1} , the likely cause of this being a sp^3 bonded carbon along the edge site of the defect. From this, it is hypothesized that this mode will be observed primarily for defects near edge sites that maintain sp^2 character throughout.

In addition to the peak near 1530 cm^{-1} , two considerably more pronounced E_{2g} peaks near 1650 cm^{-1} are present in the DPD-III spectra. These peaks have been observed in simulations by Kudin et al. [49] for a 5-7-7-5 type Stone-Wales defect in graphite (see DPD-III in Figure 7 for a 5-8-5 example of this defect). This result is also in agreement with simulated and experimental spectra of cyclooctane ring systems presented by Menivaera et al. [69]. The first peak results from asymmetric stretches in the pentane and hexane rings coupled to a breathing mode present in the octane ring. The second peak results from strong asymmetric vibrations along the pentane-octane-pentane edge of the system. Several low to moderate intensity peaks are present between 1000 cm^{-1} and 1200 cm^{-1} , these vibrations are a result of circular breathing of the octane ring system and are in good agreement with previous results [69]. Surprisingly, no peaks are observed near 1450 cm^{-1} in relation to the pentane ring system, but this effect is most likely due to restriction of Kekulé vibrations in the adjacent hexagonal rings.

The lack of symmetry and the presence of two sp^3 hybridized carbon in the DPD-II system results in a complex Raman spectrum that contains a number of strong vibrational modes, the strongest being combined semi-circular breathing modes for the pentane and hexane rings near 1400 cm^{-1} , followed by assorted breathing modes and Kekulé vibrations of the three-ring, phenanthrene-like, region near 1200 cm^{-1} and 1340 cm^{-1} respectively. Breathing modes and asymmetric stretch modes mix to produce a moderately intense band near 1470 cm^{-1} as well. Numerous asymmetric stretch modes are observed between 1500 cm^{-1} and 1600 cm^{-1} , with those near 1500 cm^{-1} resulting from unconstrained carbons surrounding the defect, and modes near 1600 cm^{-1} originating primarily in the phenanthrene-like fragment. The final peak near 1650 cm^{-1} ,

as with the heptane centered ring system, results from constrained semi-circular breathing of the large ring system mixed with asymmetric stretching in the surrounding rings.

In each defect examined, save nitrogen inclusion, a moderate decrease in frequency (red shift) was noted for the primary asymmetric stretch mode. This red shift becomes continually more pronounced as ring deformation increases. A similar effect has been observed in single layer graphene when subjected to out of plane strain [70, 71]. Combined, these results suggest that strained deformations of polycyclic clusters are a primary cause of the commonly observed asymmetry in the G-band of chars and activated carbons.

3.3.4 Computational study on the effect of oxygenated groups in defects and at edge sites

Oxygen substitution at point defects, shown in Figure 9, results in many of the same type of spectral shifts previously discussed. The oxygenated defects do not appear to strongly affect the breathing and Kekulé modes between 1200 and 1400 cm^{-1} beyond the effects already observed for non-oxygenated defects. The inclusion of oxygen was, however, found to result in significant alterations of the asymmetric stretching modes. A strong red shift in the position of the primary asymmetric stretch mode for SPD-O-I and II as well as DPD-O-II was observed. This shift is the result of moderate mixing of asymmetric stretches with the assorted breathing modes in one or more benzene rings. By contrast, neither DPD-O-I or III showed significant red shift of the asymmetric band. The oxygen defect in both systems causes relatively little constriction within the vibrations of the carbon structure, as compared to the other oxygenated defects. Because of this, mixing of the asymmetric and breathing modes was substantially less prevalent, though a distribution of asymmetric modes resulted in a more distributed G-band region for both compounds.

The vibrational shifts observed suggest that the presences of oxygen in a deformed PAH results in the same G-band red shift as for non-oxygenated systems, though the degree of the shift appears to be more intense. The spectra reported by Gokus et al. [72] for the treatment of graphene by oxygen plasma resulted in not only the formation of a D-band, but a significant red shifted asymmetry in the G-band, consistent with this hypothesis. Wang et al. [73] also assigned

a peak that developed near 1550 cm^{-1} to oxygenated compounds after electrochemical pretreatment of graphite in HNO_3 , while simulations by Kudin [49] also identified similar red shifts for oxygenated graphite.

As seen in Figure 10, the effect of oxygen on the Raman spectrum of PAHs is less pronounced when edge sites are modified rather than inserted as defects, which break the conjugated structure. The accuracy of these calculations was evaluated by comparison of simulated and experimental spectra of tetracarboxylic perylene (excited at 1064 nm). This comparison demonstrates accurate relative intensity reproduction as well as consistent frequencies after correction. The spectral changes observed for edge modified coronene systems can also be partially understood in terms of symmetry reduction; while the parent coronene is D_{6h} , the derivatives are each reduced to the C_s point group (mirror plane only). As the symmetry is lowered due to substitution, degeneracies are lifted and forbidden modes become allowed. Despite the lowering of all derivatives to the same point group, significantly stronger effects were observed for systems containing double-bonded oxygen attached directly to the aromatic structure as seen with the inclusion of a carbonyl group or a lactone group. While multiple additional peaks were present in each system, only those present in the lactone and carbonyl modified groups achieved significant intensity compared to the parent coronene peaks. This effect appears to be a result of charge distribution near the oxygen. Double bonded oxygen systems more strongly affect the electron distribution across the ring systems, constraining movement of the adjacent carbon in breathing modes near 1350 cm^{-1} . Restriction of this carbon motion results in the formation of strong secondary peaks. Such peak splitting is likely to be observed as generalized broadening of the D-band, rather than the development of defined peaks in heterogeneous systems such as char. This effect is substantially less pronounced in both the hydroxyl and carboxyl modified systems, which, by comparison, have only minor effects on the charge distribution of the adjacent carbon. Double bonded oxygen groups (carbonyls) can be easily identified by a distinctive stretch present at 1700 cm^{-1} (free carbonyl) to 1800 cm^{-1} (carboxyl/lactone), in line with typical frequencies in organic compounds [74].

In addition to the coronene based spectra that have been presented, a selection of defects were also analyzed for circumpyrene and circumcoronene parent rings. The effects of defects within

these systems were found to be in agreement with the results presented for coronene. Details of these spectra can be seen in Figures S1 and S2 in the supplemental material.

3.5 Band assignments from simulation results

Simulations of several different PAHs in the previous section have provided significant insight to the complex Raman spectra of amorphous carbons such as chars and activated carbons. The results of these studies are summarized in Table 4 with detailed descriptions of each band provided below.

Shoulder band, Low (S_L) ($975\text{-}1075\text{ cm}^{-1}$): Each small PAH tested was found to have weak symmetric breathing mode vibrations between 975 cm^{-1} and 1075 cm^{-1} (see Figure 4). The observed vibrational modes in this region are coupled to hydrogen motion along the periphery, but, with the exception of the mode for naphthalene, these vibrations were generally very minor compared to the rest of the spectra. Also identified within this region is a strong secondary symmetric vibration for the cycloheptane centered molecule near 1000 cm^{-1} (see Figure 6B). This mode is also observed for larger cyclic rings such as cyclooctane [69]. Vibrations within these regions have previously been documented [48] for pure PAHs but are typically too weak to identify in chars and activated carbons [16, 43, 44].

Shoulder band (S) ($1150\text{-}1200\text{ cm}^{-1}$): Breathing modes of cyclic systems containing 7 membered rings have been observed within this region for modelled systems (figure 6B). Literature reports also cite similar modes for systems containing cyclooctanes [69]. Aromatic rings of a size similar to pyrene display symmetric breathing modes within this region, these modes are also present in defective clusters such as SPD-II and DPD-II (Figures 7 and 8 respectively) that contain small aromatic moieties. The presence of heteroatoms in adjacent rings was not found to forbid these modes (Figure 9). Intensity in this region has previously been linked to aliphatic TPA type groups; however, the simulations conducted here identified no compelling evidence that this is the primary mode associated with the shoulder in PAH ring systems (see Figure 5).

Defect bands (D_s and D) (1250- 1300 cm^{-1} and 1325-1375 cm^{-1}): Vibrations within these regions are ascribed to a mixture of symmetric breathing modes and Kekulé type vibrations in larger ring systems. These modes become strongly enhanced in highly ordered systems due to degeneracy as well as resonant effects with the incident light [37]. In smaller systems with lower order symmetry, multiple vibrational modes exists due to coupling of breathing and Kekulé modes. These modes are red and blue shifted from the expected peak at 1350 cm^{-1} . For small PAHs this can result in the formation of two distinct peaks, the first between 1250 cm^{-1} and 1300 cm^{-1} (D_s), and the second between 1370 cm^{-1} and 1400 cm^{-1} as can be seen in the spectra of perylene and benzo[g,h,i]perylene in Figure 4. Complicating the analysis of this region, combinations of breathing and Kekulé modes have been found to result in a strong D-band, with a moderate secondary mode near 1250 cm^{-1} (D_s) and a weak shoulder near 1360 cm^{-1} for larger aromatic systems [50, 51]. In addition, the work of Negri et al. [50] suggests that linearly arranged, Rylene-type, molecules show increased intensity near 1250 cm^{-1} as the total chain length increases. A general trend observed for systems larger than coronene is a gradual reduction in relative intensity for the primary breathing mode (D), as demonstrated by Negri et al. [50] and observed with both circumpyrene and circumcoronene in our calculations (Supplemental Figures S1 and S2).

Amorphous bands (A_1 and A_2) (1400-1460 cm^{-1} and 1480-1550 cm^{-1}): Uncertainty has remained in the assignment of the A-band within the literature. However, sources generally agree that this valley region is related to irregular structures [16, 43]. Here we identify two distinct bands, the first (A_1) is found between 1400-1460 cm^{-1} and is assigned primarily to Kekulé dominated vibrations coupled to symmetric breathing of an adjacent cyclopentane ring. This is most clearly demonstrated by the cyclopentane centered system shown in Figure 6A and is consistent with both experimental and calculated spectra for C60 fullerenes [68, 75]. Evidence of this effect is also present in several point defect systems such as SPD-II and SPD-III (Figure 7) and DPD-II (Figure 8). The 5-8-5 Stone-Wales defect in DPD-III did not show this band however.

The second band (A_2) is a mixture of breathing and asymmetric stretching modes of ring systems adjacent to point defects and is seen most prominently as moderate to intense vibrational modes between 1500 cm^{-1} and 1550 cm^{-1} as seen in the spectra for the cycloheptane center

cluster, SPD-III, DPD-I and DPD-III (see Figures 6-8). The results of this study suggest that this region is strongly linked to out of plane deformation around defects. A second origin for this band involves heteroatom (specifically oxygen) defects. These defects partially restrict asymmetric stretch modes resulting in mixing with breathing modes. The net effect is a strong red shift to approximately 1480 cm^{-1} of the primary asymmetric bands in heavily restricted systems (see Figure 9). Both the presence of heteroatoms and large out of plane bends resulted in larger red shifts of the primary E_{2g} related mode, though oxygenated defects resulted in substantially greater red shifts. Inclusion of nitrogen was found to have similar, albeit substantially less intense effect on the formation of a mixed breathing-asymmetric stretch modes (see Figure 7).

Graphitic bands (G_g and G_L) ($1570\text{-}1600\text{ cm}^{-1}$): The G-band represents vibrational modes associated with the asymmetric stretch of various sp^2 carbons [40], and is represented by the E_{2g} stretch shown in Figure 4D. While asymmetric stretching occurs in this region for a wide range of compounds, the structure of molecule and the overall symmetry of the system play an important role in the distribution of the vibrations, as can be seen in Figures 4 -10. To account for the varying effects of defects and PAH cluster size on the G-band, this region has been assumed to result from two overlapping bands. The first band, G_G , is assigned a Gaussian profile and represents small PAHs and defects that produce a distribution of fragmented peaks concentrated in the 1550 cm^{-1} to 1650 cm^{-1} region. The second band, G_L , is assigned a Lorentzian profile and represents medium to large ring clusters, as larger groups show a single sharp band with minimal distribution located near 1600 cm^{-1} . These assignments have been made based on the theory that vibrational bands that arise from localized or only locally-distributed modes, such as those in graphite, are best represented by a Lorentzian style peak [40, 41], whereas Gaussian peaks better represent statistical distributions of different vibrational states, i.e. an inhomogeneous broadening mechanism [76, 77]. The distribution between these peaks is used in this analysis to qualitatively assess the overall character of the char.

D' band ($1605\text{-}1650\text{ cm}^{-1}$): In this study, the D' band is related to the process of a central ring breathing mode with surrounding asymmetric stretch behavior. This mode was only significant

for coronene (Figure 4A) and the cycloheptane centered ring system (Figure 6B). The frequency and relative intensity of this band are well predicted for coronene by the simulation.

Carbonyl stretch (C)-band (1750-1800 cm^{-1}): Each simulated compound containing a carbonyl group shows a band located between 1700 cm^{-1} and 1800 cm^{-1} (see Figure 9), consistent with reported values [78]. The experimental spectrum from tetracarboxylic perylene (dashed red overlay in Figure 9) confirms the location and intensity predicted for this band by the DFT simulations.

3.6 Deconvolution of Dispersive Raman Spectra from Cellulose derived Chars

Figure 11 shows the Raman spectra of cellulose derived chars obtained between 400 °C and 700 °C. Pyrolysis temperature can be seen to strongly affect the final Raman spectra of chars from cellulose, indicating significant differences do exist in the overall char structure. The results obtained from deconvolution of each spectrum are consistent with changes in cluster size, defects and composition and strongly indicate increasing ordering within the system as well as a reduction in oxygen content as pyrolysis temperature is increased. The central D-band position is found to shift substantially, moving from 1380 cm^{-1} to 1340 cm^{-1} with increasing pyrolysis temperature. The overall position of the shoulder near 1250 cm^{-1} does not appear to move significantly, though overall intensity of this mode decreases with pyrolysis temperature. The G-band shows consistent narrowing with temperature, with a sharp drop in the valley intensity between the G-band and D-band (the A-band region) as pyrolysis temperature was increased from 400 °C to 600 °C. At 700 °C an increase in the minimum valley intensity is observed as well as moderate broadening of the G-band.

The dispersive Raman spectrum of cellulose char produced at 400 °C, shown in Figure 12A, exemplifies the difficulty in curve fitting spectra from pyrolysis chars. The band assignments given in table 4 have been used to deconvolute and analyze the complex spectra of these materials. The results from this study indicate a complex material structure containing a multitude of small PAH systems, ether groups and an assortment of non-hexagonal ring systems. The structural features identified by the band assignments are qualitatively consistent with low

temperature char models such as the coal model presented by Shinn [32] and reproduced in Figure 1C. The position and intensity of the peaks used to deconvolute the Raman spectra of cellulose chars produced between 400 °C and 700 °C are shown in Figure 12B-D. Figure 12B highlights changes in peak positions for S, D and A bands, while Figures 12C and 12D show changes in peak intensities for breathing/Kekulé and asymmetric stretch dominated bands respectively. Table 5 details changes in peak width with pyrolysis temperature.

The peak area ratios for each band as compared to the summation of the G_G and G_L bands (G_T) are provided in Table 6. The ratio $I(D)/I(G_T)$ follows the same increasing trend with temperature observed by McDonald-Wharry et al. [16] for pyrolysis chars, though the observed ratios are lower in this report. It is noted that we utilize the total peak area for this analysis while McDonald-Wharry et al. used maximum peak intensities. The summation of the S, D_S , D, and A_1 peaks (D^*) the D band region typically obtained by a two curve deconvolution can be approximated. The G-band for this method can be approximated by the summation of G_G , G_L , and A_2 (G^*). Examining the $I(D^*)/I(G^*)$ ratios reveals trends consistent with the $I(D)/I(G_T)$ ratio. The same trends are also observed when examining the intensity ratios of only the summed D_S and D peaks ($I(D_T)/(G_T)$), indicating that the growth of the D-band is the controlling parameter within this region. The $I(D^*)/I(G^*)$ ratios observed for each char, and the known structure of these materials, place all of chars within the hysteresis region between amorphous carbon and nano-crystalline graphite and are consistent with an ordering trajectory as discussed by Ferrari and Robertson [40]. The intensity ratios of other bands are consistent with the raw intensities show in figure 12C and 12D.

The clearest changes observed as processing temperatures increase are concentrated in the D and G-bands. A red shift in the D-band peak position is accompanied by moderate band broadening, increasing by approximately 20% over the temperature range studied. The total intensity also increases by 50% over this temperature range. The red shift in peak position of the D-band is consistent with the formation of larger aromatic clusters. The identified D-bands shifts from approximately 1380 cm^{-1} (where bands from small compounds such as pyrene and perylene dominate) for chars produced at 400 °C to 1340 cm^{-1} at 700 °C, much more in accordance with the breathing mode of coronene and larger PAH molecules [50, 51]. The D_S band is assigned to

assorted breathing modes in various PAHs. The peak position for chars produced at 400 °C is located at approximately 1275 cm⁻¹, well within the observed range of these modes. As temperature increase, the position of this peaks moves towards 1250 cm⁻¹ with consistent decreases in intensity. This result, coupled with the behavior of the primary D peak is consistent with the formation of moderately sized (coronene like) PAHs. These results do not exclude the formation of larger aromatic systems, however such systems would be expected to be less prevalent within the structure.

Changes in the G-band also are consistent with the formation of larger, less distorted ring systems as the pyrolysis temperature increases. The Gaussian character initially observed in the 400 °C char gives way to a much stronger Lorentzian profile at 700 °C. This change occurs sharply at treatment temperatures of 500 °C and continues more gradually as temperature increases further. Trends in both the D-band and G-band are consistent with results previously published on the effect of temperature on char spectra [16, 44].

The consistent decrease in intensity observed in the A₂ band as temperature increases from 400-600 °C, combined with the relatively low peak position near 1510 cm⁻¹ suggests that oxygenated defects contributed to the intensity of this region for chars produced at temperatures lower than 700 °C. Numerous oxygen groups are at least partially stable in this temperature regime, only decomposing fully at temperatures approaching 650 °C [30].

The apparent decrease and subsequent increase of the S-band with temperature suggests that at least two distinct structures contribute to this band. Intensity within this region may be partially due to TPA type regions in chars produced at 400 °C, with degradation of these moieties upon heating to 500 °C explaining the reduction in peak intensity. The increase observed after heating to 700 °C is hypothesized to be a result of the formation of cycloheptane and larger ring systems as the char structure condenses (Figure 6B). Evidence for these structures has been observed in high-resolution transmission electron microscopy (HRTEM) images by Harris et al. [28, 29]. Given the moderately intense breathing mode identified near 1180 cm⁻¹ (see Figure 6B) for this structure, it is suspected that cycloheptanes increasingly contribute to the S-band observed in chars produced at temperatures greater than 500 °C.

The major peak identified near 1450 cm^{-1} is correlated to Kekulé dominated vibrations in small PAH clusters, as well as mixed breathing and Kekulé modes in systems containing 5-membered rings. The A_1 band was found to be highly stable with temperature, consistently identified between 1450 cm^{-1} and 1460 cm^{-1} . Increasing temperature resulted in both an increase in intensity as well as peak width. The position of the band suggests that Kekulé vibrations coupled with the A_{1g} mode of cyclopentane rings is the primary origin of intensity within this region. Small PAH systems without pentane rings would be expected to show greater intensity near 1400 cm^{-1} and decrease with temperature. This result suggests that as the pyrolysis temperature increases pentane ring systems become more prevalent within the cellulose char.

Analysis of the S_L , D' and C bands was not possible due the minimal intensities of these features.

4 Conclusions

The theoretical gas-phase Raman spectra of a variety of ordered and defective PAHs have been analyzed. The experimental spectra of several model compounds were used to validate appropriate frequency scaling factors and visualize important Raman active vibrations. Key vibrational modes of various defects were analyzed for distinctive regions to create a new series of band assignments specifically tailored for chars produced at temperatures below $700\text{ }^{\circ}\text{C}$. Our results have shown that the shoulder peak identified near 1200 cm^{-1} is consistent with vibrational modes for PAH structures, specifically, symmetric breathings modes of cycloheptane and larger ring systems which form between 1150 cm^{-1} and 1200 cm^{-1} . The breathing modes of small PAHs (Naphthalene-pyrene scale) were found to be present between 1200 cm^{-1} and 1300 cm^{-1} as well as for larger ring systems (greater than coronene). We have demonstrated that the valley commonly observed in Raman spectra and chars is consistent with the modeled system disorder. Intensity between 1400 cm^{-1} and 1450 cm^{-1} has been assigned to Kekulé dominated vibrational modes, especially those coupled to breathing modes of pentane ring systems. Intensity between 1480 cm^{-1} and 1550 cm^{-1} , typically observed as an asymmetric G-band, is linked to coupling of breathing modes and asymmetric stretching caused by strained deformation within the PAH clusters and constriction of motion caused by oxygen inclusion. The new fitting parameters

provided excellent fits of each char, but care must be taken to avoid peak divergence, as a sufficient number of fitting parameters are provided for non-meaningful deconvolutions to occur. Analysis of changes in peak parameters with increasing temperature reveal trends consistent with cluster growth, loss of internal oxygenated structures, and formation of non-hexagonal ring systems within the char samples.

Acknowledgements:

The authors are very thankful for the financial support provided by the US National Science Foundation (CBET-1434073, CAREER CBET-1150430), the Washington State Department of Ecology, and the Washington State Department of Agriculture (Appendix A). It was also partially funded by the USDA/NIFA through Hatch Projects #WNP00807 and # WNP00701. Part of the research described in this paper was supported in part by the U. S. Department of Energy. PNNL is operated by Battelle for the U.S. DOE under Contract DE-AC05-76RLO1830. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of the manuscript, or allow others to do so, for United States Government purposes. JFE thanks partial support from the “Programa Sostenibilidad 2014-2015” of the University of Antioquia.

References:

- [1] Antal MJ, Gronli M. The Art, Science, and Technology of Charcoal Production†. *Industrial & Engineering Chemistry Research*. 2003;42(8):1619-40.
- [2] Peláez-Samaniego MR, Garcia-Perez M, Cortez LB, Rosillo-Calle F, Mesa J. Improvements of Brazilian carbonization industry as part of the creation of a global biomass economy. *Renewable and Sustainable Energy Reviews*. 2008;12(4):1063-86.
- [3] Lehmann J, Joseph S. Biochar for Environmental Management: An Introduction. In: Lehmann J, Joseph S, editors. *Biochar for Environmental Management: Science and Technology*. Washington DC: Earthscan 2009. p. 1-9.

- [4] Woolf D, Amonette JE, Street-Perrott FA, Lehmann J, Joseph S. Sustainable biochar to mitigate global climate change. *Nat Commun.* 2010;1:56.
- [5] Solomon D, Lehmann J, Thies J, Schäfer T, Liang B, Kinyangi J, et al. Molecular signature and sources of biochemical recalcitrance of organic C in Amazonian Dark Earths. *Geochimica et Cosmochimica Acta.* 2007;71(9):2285-98.
- [6] Lehmann J, Gaunt J, Rondon M. Bio-char Sequestration in Terrestrial Ecosystems – A Review. *Mitigation and Adaptation Strategies for Global Change.* 2006;11(2):395-419.
- [7] Matovic D. Biochar as a viable carbon sequestration option: Global and Canadian perspective. *Energy.* 2011;36(4):2011-6.
- [8] Glaser B, Lehmann J, Zech W. Ameliorating Physical and Chemical Properties of Highly Weathered Soils in the Tropics with Charcoal - a Review. *Biology and Fertility of Soils.* 2002;35:219-30.
- [9] Blackwell P, Riethmuller G, Collins M. Biochar Application to Soil. In: Lehmann J, Joseph S, editors. *Biochar for Environmental Management: Science and Technology.* Washington DC: Earthscan 2009. p. 207-26.
- [10] Ahmad M, Rajapaksha AU, Lim JE, Zhang M, Bolan N, Mohan D, et al. Biochar as a sorbent for contaminant management in soil and water: A review. *Chemosphere.* 2014;99:19-33.
- [11] Mohan D, Sarswat A, Ok YS, Pittman Jr CU. Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent – A critical review. *Bioresour Technol.* 2014;160:191-202.
- [12] Pandolfo AG, Hollenkamp AF. Carbon properties and their role in supercapacitors. *J Power Sources.* 2006;157(1):11-27.
- [13] Wu YP, Rahm E, Holze R. Carbon anode materials for lithium ion batteries. *J Power Sources.* 2003;114(2):228-36.
- [14] Alcántara R, Jiménez-Mateos JM, Lavela P, Tirado JL. Carbon black: a promising electrode material for sodium-ion batteries. *Electrochem Commun.* 2001;3(11):639-42.
- [15] Ponrouch A, Goñi AR, Palacín MR. High capacity hard carbon anodes for sodium ion batteries in additive free electrolyte. *Electrochem Commun.* 2013;27:85-8.

- [16] McDonald-Wharry J, Manley-Harris M, Pickering K. Carbonisation of biomass-derived chars and the thermal reduction of a graphene oxide sample studied using Raman spectroscopy. *Carbon*. 2013;59:383-405.
- [17] Li X, Hayashi J-i, Li C-Z. Volatilisation and catalytic effects of alkali and alkaline earth metallic species during the pyrolysis and gasification of Victorian brown coal. Part VII. Raman spectroscopic study on the changes in char structure during the catalytic gasification in air. *Fuel*. 2006;85(10-11):1509-17.
- [18] Tsechansky L, Graber ER. Methodological limitations to determining acidic groups at biochar surfaces via the Boehm titration. *Carbon*. 2014;66(0):730-3.
- [19] Franklin RE. Crystallite Growth in Graphitizing and Non-Graphitizing Carbons. *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*. 1951;209(1097):196-218.
- [20] Brewer CE, Schmidt-Rohr K, Satrio JA, Brown RC. Characterization of biochar from fast pyrolysis and gasification systems. *Environmental Progress & Sustainable Energy*. 2009;28(3):386-96.
- [21] Cao X, Pignatello JJ, Li Y, Lattao C, Chappell MA, Chen N, et al. Characterization of Wood Chars Produced at Different Temperatures Using Advanced Solid-State ¹³C NMR Spectroscopic Techniques. *Energy & Fuels*. 2012;26(9):5983-91.
- [22] Demirbaş A. Mechanisms of liquefaction and pyrolysis reactions of biomass. *Energy Convers Manage*. 2000;41(6):633-46.
- [23] Chaiwat W, Hasegawa I, Tani T, Sunagawa K, Mae K. Analysis of cross-linking behavior during pyrolysis of cellulose for elucidating reaction pathway. *Energy & Fuels*. 2009;23(12):5765-72.
- [24] Mohan D, Pittman CU, Steele PH. Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review. *Energy & Fuels*. 2006;20(3):848-89.
- [25] McGrath TE, Chan WG, Hajaligol MR. Low temperature mechanism for the formation of polycyclic aromatic hydrocarbons from the pyrolysis of cellulose. *Journal of Analytical and Applied Pyrolysis*. 2003;66(1-2):51-70.
- [26] Wang Z, Pecha B, Westerhof RJM, Kersten SRA, Li C-Z, McDonald AG, et al. Effect of Cellulose Crystallinity on Solid/Liquid Phase Reactions Responsible for the Formation of

- Carbonaceous Residues during Pyrolysis. *Industrial & Engineering Chemistry Research*. 2014;53(8):2940-55.
- [27] Kersten S, Garcia-Perez M. Recent developments in fast pyrolysis of ligno-cellulosic materials. *Current Opinion in Biotechnology*. 2013;24(3):414-20.
- [28] Harris PJF, Liu Z, Suenaga K. Imaging the atomic structure of activated carbon. *Journal of Physics: Condensed Matter*. 2008;20(36):362201.
- [29] Harris PJF. New Perspectives on the Structure of Graphitic Carbons. *Crit Rev Solid State Mater Sci*. 2005;30(4):235-53.
- [30] Kundu S, Wang Y, Xia W, Muhler M. Thermal Stability and Reducibility of Oxygen-Containing Functional Groups on Multiwalled Carbon Nanotube Surfaces: A Quantitative High-Resolution XPS and TPD/TPR Study. *The Journal of Physical Chemistry C*. 2008;112(43):16869-78.
- [31] Shen W, Li Z, Liu Y. Surface Chemical Functional Groups Modification of Porous Carbon. *Recent Patents on Chemical Engineering*. 2008;1(1):27-40.
- [32] Shinn JH. From coal to single-stage and two-stage products: A reactive model of coal structure. *Fuel*. 1984;63(9):1187-96.
- [33] Carlson GA. Computer simulation of the molecular structure of bituminous coal. *Energy & Fuels*. 1992;6(6):771-8.
- [34] Palmer JC, Gubbins KE. Atomistic models for disordered nanoporous carbons using reactive force fields. *Microporous and Mesoporous Materials*. 2012;154:24-37.
- [35] Tuinstra F, Koenig JL. Raman Spectrum of Graphite. *The Journal of Chemical Physics*. 1970;53(3):1126-30.
- [36] Vidano RP, Fischbach DB, Willis LJ, Loehr TM. Observation of Raman band shifting with excitation wavelength for carbons and graphites. *Solid State Commun*. 1981;39(2):341-4.
- [37] Thomsen C, Reich S. Double Resonant Raman Scattering in Graphite. *Physical Review Letters*. 2000;85(24):5214-7.
- [38] Reich S, Thomsen C. Raman spectroscopy of graphite. *Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*. 2004;362(1824):2271-88.

- [39] Pimenta MA, Dresselhaus G, Dresselhaus MS, Cancado LG, Jorio A, Saito R. Studying disorder in graphite-based systems by Raman spectroscopy. *Physical Chemistry Chemical Physics*. 2007;9(11):1276-90.
- [40] Ferrari AC, Robertson J. Raman spectroscopy of amorphous, nanostructured, diamond-like carbon, and nanodiamond. *Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*. 2004;362(1824):2477-512.
- [41] Ferrari AC, Basko DM. Raman spectroscopy as a versatile tool for studying the properties of graphene. *Nat Nano*. 2013;8(4):235-46.
- [42] Ferrari AC, Robertson J. Interpretation of Raman spectra of disordered and amorphous carbon. *PhRvB*. 2000;61(20):14095-107.
- [43] Hu C, Sedghi S, Silvestre-Albero A, Andersson GG, Sharma A, Pendleton P, et al. Raman spectroscopy study of the transformation of the carbonaceous skeleton of a polymer-based nanoporous carbon along the thermal annealing pathway. *Carbon*. 2015;85:147-58.
- [44] Yamauchi S, Kurimoto Y. Raman spectroscopic study on pyrolyzed wood and bark of Japanese cedar: temperature dependence of Raman parameters. *J Wood Sci*. 2003;49(3):235-40.
- [45] Zickler GA, Smarsly B, Gierlinger N, Peterlik H, Paris O. A reconsideration of the relationship between the crystallite size L_a of carbons determined by X-ray diffraction and Raman spectroscopy. *Carbon*. 2006;44(15):3239-46.
- [46] Becke AD. Perspective: Fifty years of density-functional theory in chemical physics. *The Journal of Chemical Physics*. 2014;140(18):18A301.
- [47] Cheeseman JR, Frisch MJ. Basis Set Dependence of Vibrational Raman and Raman Optical Activity Intensities. *Journal of Chemical Theory and Computation*. 2011;7(10):3323-34.
- [48] Shinohara H, Yamakita Y, Ohno K. Raman spectra of polycyclic aromatic hydrocarbons. Comparison of calculated Raman intensity distributions with observed spectra for naphthalene, anthracene, pyrene, and perylene. *J Mol Struct*. 1998;442(1-3):221-34.
- [49] Kudin KN, Ozbas B, Schniepp HC, Prud'homme RK, Aksay IA, Car R. Raman Spectra of Graphite Oxide and Functionalized Graphene Sheets. *Nano Lett*. 2008;8(1):36-41.
- [50] Negri F, Castiglioni C, Tommasini M, Zerbi G. A Computational Study of the Raman Spectra of Large Polycyclic Aromatic Hydrocarbons: Toward Molecularly Defined Subunits of Graphite†. *The Journal of Physical Chemistry A*. 2002;106(14):3306-17.

- 969 [51] Castiglioni C, Mapelli C, Negri F, Zerbi G. Origin of the D line in the Raman spectrum of
970 graphite: A study based on Raman frequencies and intensities of polycyclic aromatic
971 hydrocarbon molecules. *The Journal of Chemical Physics*. 2001;114(2):963-74.
- 972 [52] Bonen D, Johnson TJ, Sarkar SL. Characterization of principal clinker minerals by FT-
973 Raman microspectroscopy. *Cement and Concrete Research*. 1994;24(5):959-65.
- 974 [53] Johnson TJ, Su Y-F, Jarman KH, Kunkel BM, Birnbaum JC, Joly AG, et al. Demonstrated
975 Wavelength Portability of Raman Reference Data for Explosives and Chemical Detection.
976 *International Journal of Spectroscopy*. 2012;2012:11.
- 977 [54] Williams S, Johnson T, Gibbons T, Kitchens C. Relative Raman Intensities in C₆H₆, C₆D₆,
978 and C₆F₆: A Comparison of Different Computational Methods. *Theor Chem Acc*.
979 2007;117(2):283-90.
- 980 [55] Menéndez JA, Phillips J, Xia B, Radovic LR. On the Modification and Characterization of
981 Chemical Surface Properties of Activated Carbon: In the Search of Carbons with Stable
982 Basic Properties. *Langmuir*. 1996;12(18):4404-10.
- 983 [56] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et al.
984 Gaussian 09, Revision B.01. Wallingford CT2009.
- 985 [57] Becke AD. Density-functional thermochemistry. III. The role of exact exchange. *The*
986 *Journal of Chemical Physics*. 1993;98(7):5648-52.
- 987 [58] Hariharan PC, Pople JA. The influence of polarization functions on molecular orbital
988 hydrogenation energies. *AcTC*. 1973;28(3):213-22.
- 989 [59] Dunning TH. Gaussian basis sets for use in correlated molecular calculations. I. The atoms
990 boron through neon and hydrogen. *The Journal of Chemical Physics*. 1989;90(2):1007-23.
- 991 [60] Kendall RA, Dunning TH, Harrison RJ. Electron affinities of the first-row atoms revisited.
992 Systematic basis sets and wave functions. *The Journal of Chemical Physics*.
993 1992;96(9):6796-806.
- 994 [61] Yoshida H, Ehara A, Matsuura H. Density functional vibrational analysis using
995 wavenumber-linear scale factors. *Chem Phys Lett*. 2000;325(4):477-83.
- 996 [62] Rauhut G, Pulay P. Transferable Scaling Factors for Density Functional Derived Vibrational
997 Force Fields. *The Journal of Physical Chemistry*. 1995;99(10):3093-100.

- [63] Halls MD, Velkovski J, Schlegel HB. Harmonic frequency scaling factors for Hartree-Fock, S-VWN, B-LYP, B3-LYP, B3-PW91 and MP2 with the Sadlej pVTZ electric property basis set. *Theor Chem Acc.* 2001;105(6):413-21.
- [64] Schmidt JR, Polik WF. WebMO Enterprise. Holland, MI, USA: WebMO LLC; 2013.
- [65] Ferrari AC, Robertson J. Origin of the **1150-cm⁻¹** Raman mode in nanocrystalline diamond. *Physical Review B.* 2001;63(12):121405.
- [66] Ito T, Shirakawa H, Ikeda S. Thermal cis-trans isomerization and decomposition of polyacetylene. *Journal of Polymer Science: Polymer Chemistry Edition.* 1975;13(8):1943-50.
- [67] Meilunas R, Chang RPH, Liu S, Jensen M, Kappes MM. Infrared and Raman spectra of C60 and C70 solid films at room temperature. *J Appl Phys.* 1991;70(9):5128-30.
- [68] Chase B, Herron N, Holler E. Vibrational spectroscopy of fullerenes (C60 and C70). Temperature dependant studies. *The Journal of Physical Chemistry.* 1992;96(11):4262-6.
- [69] Minaeva VA, Minaev BF, Baryshnikov GV, Ågren H, Pittelkow M. Experimental and theoretical study of IR and Raman spectra of tetraoxa[8]circulenes. *Vibrational Spectroscopy.* 2012;61:156-66.
- [70] Huang M, Yan H, Chen C, Song D, Heinz TF, Hone J. Phonon softening and crystallographic orientation of strained graphene studied by Raman spectroscopy. *Proceedings of the National Academy of Sciences.* 2009;106(18):7304-8.
- [71] Mohiuddin TMG, Lombardo A, Nair RR, Bonetti A, Savini G, Jalil R, et al. Uniaxial strain in graphene by Raman spectroscopy: *G* peak splitting, Grüneisen parameters, and sample orientation. *Physical Review B.* 2009;79(20):205433.
- [72] Gokus T, Nair RR, Bonetti A, Böhmmler M, Lombardo A, Novoselov KS, et al. Making Graphene Luminescent by Oxygen Plasma Treatment. *ACS Nano.* 2009;3(12):3963-8.
- [73] Wang Y, Alsmeyer DC, McCreery RL. Raman spectroscopy of carbon materials: structural basis of observed spectra. *Chem Mater.* 1990;2(5):557-63.
- [74] Lin-Vien D, Colthup NB, Fateley WG, Grasselli JG. The handbook of infrared and Raman characteristic frequencies of organic molecules: Elsevier; 1991.
- [75] Schettino V, Pagliai M, Cardini G. The Infrared and Raman Spectra of Fullerene C70. DFT Calculations and Correlation with C60. *The Journal of Physical Chemistry A.* 2002;106(9):1815-23.

- 1029 [76] Sadezky A, Muckenhuber H, Grothe H, Niessner R, Pöschl U. Raman microspectroscopy of
1030 soot and related carbonaceous materials: Spectral analysis and structural information.
1031 Carbon. 2005;43(8):1731-42.
- 1032 [77] Demtröder W. Laser Spectroscopy: Vol. 1: Basic Principles: Springer Berlin Heidelberg;
1033 2008.
- 1034 [78] Socrates G. Infrared and Raman characteristic group frequencies: tables and charts: John
1035 Wiley & Sons; 2004.

List of Tables

Table 1. Comparison of peak positions and intensities for experimental and unscaled simulated spectra of Naphthalene.

Table 2. Relative uncorrected maximum intensity of each calculated and experimental Raman spectrum as compared to the uncorrected maximum intensity peak of Naphthalene.

Table 3. Primary experimental and simulated peak positions and position errors for each major peak (normalized intensity greater than 0.1) of the PAH tested.

Table 4. Summary of peak assignments

Table 5. Peak widths at half maximum for thermoseries (cm⁻¹).

Table 6. Peak intensities compared to the total area of the G band (G_T)

Table 1. Comparison of peak positions and intensities for experimental and unscaled simulated spectra of Naphthalene.

Experimental		6-31G*		CC-pVDZ		Aug-CC-pVDZ		Aug-CC-pVDZ	
ν (cm ⁻¹)	I (arb)	ν (cm ⁻¹)	I (arb)	ν (cm ⁻¹)	I (arb)	ν (cm ⁻¹)	I (arb)	ν (cm ⁻¹)	I (arb)
391	0.07	397	0.03	398	0.03	403	0.01	397	0.01
513	0.44	520	0.19	518	0.20	521	0.13	521	0.15
724	0.01	735	0.06	730	0.02	726	0.01	730	0.01
763	0.47	777	0.30	775	0.32	773	0.34	775	0.30
1020	0.27	1056	0.21	1048	0.25	1047	0.33	1047	0.29
1147	0.10	1181	0.09	1164	0.10	1162	0.05	1174	0.04
1244	0.03	1278	0.04	1260	0.03	1249	0.03	1276	0.03
1381	1.00	1417	1.00	1417	1.00	1411	1.00	1395	1.00
1463	0.22	1509	0.43	1484	0.62	1479	0.58	1497	0.41
1576	0.21	1631	0.23	1620	0.14	1619	0.22	1612	0.20
1628	0.08	1688	0.06	1623	0.23	1668	0.08	1668	0.08
3007†	0.04	3183	1.28	3173	1.51	3171	1.12	3165	1.01
3056†	0.52	3209	2.67	3199	3.19	3196	2.42	3189	2.14
ν Error[#] (%NRMS)		2.7		1.6		1.5		1.5	
I Error^{\$} (%NRMS)		11.5		15.5		15.4		11.8	

v is frequency and **I** is relative intensity

† Data point excluded from NRMS error calculations

Data normalized to experimental peak positions

\$ Data normalized to most intense peak between 800 cm⁻¹ and 1800 cm⁻¹

for experimental and simulated spectra

Table 2. Relative uncorrected maximum intensity of each calculated and experimental Raman spectrum as compared to the uncorrected maximum intensity peak of Naphthalene.

Compound	Relative maximum intensity (naphthalene = 1)		Deviation from Experimental (%)
	Simulated	Experimental	
Naphthalene (reference)	1.0	1.0	
Pyrene	3.1	11.1	72
Perylene	19.4	16.7	16.5
Benzo[a]pyrene	5.3	7.1	25.7
Benzo[g,h,i]perylene	8	15.2	43.7
Coronene	11.8	8.4	40.0

Table 3. Primary experimental and simulated peak positions and position errors for each major peak (normalized intensity greater than 0.1) of the PAH tested.

	Vibrational Mode	Experimental		Simulated	
		ν (cm ⁻¹)	I (arb)	$\nu_{corrected}$ (cm ⁻¹)	I (arb)
Naphthalene	F. Br.	763	0.34	756	0.30
	F.Br.	1020	0.22	1027	0.21
	Kek.	1381	1.00	1378	1.00
	F. Kek.	1463	0.24	1468	0.43
	Asm. St.	1576	0.24	1586	0.23
Pyrene				1071	
	F. Br.	1066	0.22	1241	0.10
	Br.	1241	0.79	1402	1.00
	Kek.	1407	1.00	1595	0.61
	Asm. St.	1595	0.52	1640	0.63
Perylene	Asm St.	1628	0.27	971	0.62
				1302	
	F. Br	978	0.20	1370	0.07
	C. Br., Per. F. Br.	1298	0.41	1576	0.46
	C. Br., Per. Kek.	1373	0.46	1240	0.28
Benzo[a] Pyrene	Asm. St.	1570	1.00	1379	1.00
				1587	
	Br.	1237	0.61	1625	0.42
	Kek. Bnz., F. Kek. Py	1387	1.00	1640	1.00
	Asm. St. Py.	1583	0.38	1258	0.23
Benzo[g,h,i] Perylene	Asm. St. Bzn.	1622	0.31	1297	0.52
	Asm St.	1632	0.30	1379	0.47
				1608	
	Br.	1258	0.48	1350	0.25
	C. Kek., Per. F. Br.	1305	0.64	NA	0.49
Coronene	C. Br., Per. F. Kek.	1389	0.62	1609	0.47
	Asm. St.	1606	1.00	1621	1.00
				756	
	C. Br., Per. Kek.	1351	1.00	1027	1.00
	C. Br., Per. Kek	1368	0.88	1378	NA
	C. Br. Per. Asm. St.	1595	0.14	1468	0.17
	Asm. St.	1629	0.33	1586	0.33

F. = Frustrated; Br. = Breathing; Kek. = Kekulé; Asm. =Asymmetric; St. = Stretch; C = Center; Per = Peripheral; Py. = concentrated in pyrene group; Bzn. = concentrated in Benzene group

Table 4. Summary of peak assignments

Position (cm ⁻¹)	Peak	Shape	Assignment
975-1075	S _L	Gaussian	Breathing modes for small aromatic regions, secondary breathing mode for 7+ membered ring
1150-1200	S	Gaussian	breathing mode for rings containing 7+ carbons with Kekulé modes in adjacent benzene rings, benzene ring breathing modes adjacent to heteroatom defects
1250-1300	D _S	Gaussian	Assorted Breathing modes for most PAHs
1340-1380	D	Gaussian	Combined breathing/Kekulé vibrations for PAHs. Larger more symmetric systems show peaks near 1350 cm ⁻¹ , while peaks for smaller systems move towards 1400 cm ⁻¹
1400-1460	A ₁	Gaussian	Breathing mode for 5-membered rings with Kekulé vibrations in adjacent 6-membered rings and near pure Kekulé in small ring systems and moieties
1480-1550	A ₂	Gaussian	Mixed breathing and asymmetric stretch vibrational modes for sp ² carbons near defects causing out of plane deformation. Heteroatom defects tend to cause greater red shift
1570-1600	G _G	Gaussian	Distributed asymmetric vibrations for distribution of small PAHs
1570-1600	G _L	Lorentzian	Standard E _{2g} mode for large PAHs
1605-1650	D'	Gaussian	Double resonance activated breathing mode
1750-1800	C	Gaussian	Carbonyl stretching mode, very weak

Table 5. Peak widths at half maximum for thermoseries (cm⁻¹).

Peak	Pyrolysis Temperature (°C)			
	400	500	600	700
S	104.6	88.5	88.7	111.1
D _S	105.2	101.9	91.2	74.7
D	108.8	113.7	120.1	137.3
A ₁	70.1	82.6	100.2	120.6
A ₂	62.6	55.8	51.7	85.4
G _G	111.3	87.2	84	50*
G _L	65.9	81.3	73.6	95.3

*minimum peak width allowed in fitting procedure

Table 6. Peak intensities compared to the total area of the G band (G_T)

Peak	Pyrolysis Temperature ($^{\circ}\text{C}$)			
	400	500	600	700
$I(S_L)/I(G_T)$	0.05	0.05	0.04	0.05
$I(S)/I(G_T)$	0.20	0.15	0.16	0.27
$I(D_S)/I(G_T)$	0.30	0.27	0.23	0.11
$I(D)/I(G_T)$	0.52	0.56	0.69	0.98
$I(A_1)/I(G_T)$	0.14	0.22	0.29	0.35
$I(A_2)/I(G_T)$	0.14	0.09	0.05	0.19
$I(S_T)/(G_T)$	0.81	0.83	0.92	1.09
$I(D_T)/(G_T)$	0.28	0.30	0.34	0.54
$I(A_T)/(G_T)$	0.25	0.20	0.20	0.31
$I(D^*)/(G^*)$	1.01	1.10	1.31	1.43

T subscript denotes summation of related peaks

D^* is a summation of S, D_s , D, and A_1 peaks

G^* is the summation of G_G , G_L , and A_2 peaks

List of Figures:

Figure 1. Several models exist that attempt to describe the underlying structure of coals and activated carbon.

Figure 2: Application of different deconvolution methods to the Raman spectra of a cellulose pyrolysis char produced at 400 °C.

Figure 3. Effect of basis sets on the simulated Raman spectra for naphthalene. The 1064 nm experimental spectrum has been wavelength- and intensity-corrected for instrument response.

Figure 4. (A) Comparison of experimental and predicted Raman spectra for various PAHs with their position correct simulation counterparts. (B) Representation of the A_{1g} symmetric breathing mode for a benzene ring (C) Kekulé type vibration for a benzene ring (D) E_{2g} asymmetric stretch in alkene and aromatic carbons.

Figure 5. Effect of alkyl chains on the predicted Raman spectra of a coronene-based molecule.

Figure 6. (A) Effect of cyclopentane center on position of symmetric breathing mode of the parent coronene molecule in the modeled Raman spectrum (B) Predicted Raman spectra of heptane ring system at the 6-31G level, detailing a symmetric ring breathing mode near 1175 cm^{-1} .

Figure 7. Effect of various single point defects on the calculated Raman spectra of a coronene based molecule (upper spectra contains a single nitrogen atom substitution denoted in blue). The spectrum of coronene is provided at the bottom of the figure for comparison.

Figure 8. Effect of various DPDs on the calculated Raman spectra of a coronene based molecule (The spectrum of coronene is provided at the bottom of the figure for comparison).

Figure 9. Effects on the calculated Raman spectra of oxygenated single and double point defects of a coronene-based molecule. The spectrum of coronene is provided at the bottom of the figure for comparison.

Figure 10. Effect of oxygenated edge sites on the predicted Raman spectra of a coronene-based molecule. The bottom spectra are of anhydrous tetracarboxylic perylene. Solid lines represent simulated data while the dashed red line represents experimental data.

Figure 11. Experimental Raman spectra of chars produced from cellulose at different temperatures. All data were collected using a 532-nm incident light.

Figure 12. (A) Deconvolution of Raman spectra of a cellulose char produced at 400 °C using the newly proposed method.

Graphical Abstract

Figure 1. Several models exist that attempt to describe the underlying structure of coals and activated carbon, these include: (A) Representation of non-graphitizing carbon as randomly oriented nano-graphitic regions, as hypothesized by Franklin [19] (B) Illustration of the curved nature of carbon fragments containing cyclopentane-, cycloheptane- and cyclohexane-ring systems as identified by Harris et al. [28] (C) a 2D chemical representation of coal structure, as proposed by Shinn [32].

Figure 2: Application of different deconvolution methods to the Raman spectra of a cellulose pyrolysis char produced at 400 °C Fitting methods adapted from (A) Ferrari et al. [40, 42] (B) Hu et al. [43] and (C) Li et al. [17].

Figure 3. Effect of basis sets on the simulated Raman spectra for naphthalene. The 1064 nm experimental spectrum has been wavelength- and intensity-corrected for instrument response.

Figure 4. (A) Comparison of experimental and predicted Raman spectra for various PAHs with their position correct simulation counterparts. Solid black lines represent simulated results, while dashed red lines represent experimental results. (B) Representation of the A_{1g} symmetric breathing mode for a benzene ring (C) Kekulé type vibration for a benzene ring (D) E_{2g} asymmetric stretch in alkene and aromatic carbons. Position lines denoting the change in location of the A_{1g} , Kekulé and E_{2g} vibrations are provided as black lines spanning the spectra of

Naphthalene – Coronene. The symmetry labels used in 4B-D are derived from the D_{6h} structure of the benzene.

Figure 5. Effect of alkyl chains on the predicted Raman spectra of a coronene-based molecule.

Figure 6. (A) Effect of cyclopentane center on position of symmetric breathing mode of the parent coronene molecule in the modeled Raman spectrum (B) Predicted Raman spectra of heptane ring system at the 6-31G level, detailing a symmetric ring breathing mode near 1175 cm⁻¹

Figure 7. Effect of various single point defects on the calculated Raman spectra of a coronene based molecule (upper spectra contains a single nitrogen atom substitution denoted in blue). The spectrum of coronene is provided at the bottom of the figure for comparison.

Figure 8. Effect of various DPDs on the calculated Raman spectra of a coronene based molecule (The spectrum of coronene is provided at the bottom of the figure for comparison).

Figure 9. Effects on the calculated Raman spectra of oxygenated single and double point defects of a coronene-based molecule. The spectrum of coronene is provided at the bottom of the figure for comparison.

Figure 10. Effect of oxygenated edge sites on the predicted Raman spectra of a coronene-based molecule. The bottom spectra are of anhydrous tetracarboxylic perylene. Solid lines represent simulated data while the dashed red line represents experimental data.

Figure 11. Experimental Raman spectra of chars produced from cellulose at different temperatures. All data were collected using a 532-nm incident light.

Figure 12. (A) Deconvolution of Raman spectra of a cellulose char produced at 400 °C using the newly proposed method. Red line (online version only) represents the summation of curves while the solid black line is the original experimental data. The dotted black lines are individual Gaussians based on the curve fitting parameters given in Figures 13B-D and Table 5. The effect of temperature on the deconvolution curve parameters for (B) Peak position (C) Peak intensity of breathing modes and (D) peak intensity of asymmetric stretch modes are also given.

Graphical Abstract: