

Vibrational analysis of amorphous carbon-nitrogen alloys by ^{15}N and D isotopic substitution

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(Received 12 April 1999; revised manuscript received 10 August 1999)

The origin of the vibrational modes of $a\text{-CN}_x$ alloys is investigated by infrared (ir) and Raman spectroscopies. Isotopic substitution of ^{15}N and D is used in the identification of vibration modes. In *nonhydrogenated* materials containing low nitrogen concentration (≤ 20 at. %), the ir and Raman spectra are not equivalent. Above this concentration (up to ~ 30 at. %), the spectra became very similar to each other. On the contrary, for a suitable *hydrogen* content the spectra are quite similar, independently of the range of nitrogen concentrations studied. Quantum chemical Parametric Method 3 calculations are performed to obtain the frequencies and intensities of the ir active vibrations of organic molecules and large carbon-nitrogen clusters. These results are used to help in the identification of the features observed in the ir spectra. The importance of both the promotion of bond dipoles and symmetry breaking by nitrogen in the ir spectra is established.

I. INTRODUCTION

The electronic and mechanical properties of carbon-nitrogen compounds have been intensively studied during the past decade. The material is hard, showing low friction properties and is easily deposited as thin-film coating, making the material unique for technological applications.¹ Furthermore, the theoretical prediction of a crystalline C_3N_4 phase, having properties similar to those of diamond, continue to be a challenge to synthesize the material.² In spite of the large number of studies already performed, the complexity of the structure of carbon containing materials has prevented a clear understanding of several basic aspects of the alloy. For instance, most of the interpretation of the Raman and infrared (ir) spectra of carbon-nitrogen alloys ($a\text{-CN}_x$) relies on the pioneering work of Kaufman *et al.*³ These authors reported no significant changes in the Raman spectra for *hydrogenated* samples containing nitrogen between 0 and ~ 20 at. %. On the contrary, the ir spectra show profound changes as a function of nitrogen content. The conclusion of the work of Kaufman *et al.* is that the increasing ir activity stems from the fact that nitrogen breaks the symmetry of the aromatic and/or acetylene groups that constitute the material. There are two recent results to be considered when analyzing the experimental findings of Kaufman *et al.* First, the inclusion of hydrogen profoundly modifies the structure of the alloy.⁴⁻⁶ Second, above ~ 20 -at. % nitrogen content the alloy undergoes a structural change.⁷⁻⁹ The former result is particularly important since Kaufman and coworkers *exclusively* ascribe to nitrogen the changes in the ir spectra. In a previous work, however, we have shown that hydrogen modifies the ir spectra in samples containing similar amount of nitrogen and different hydrogen content.⁵ With regard to the structural changes introduced by nitrogen, the cited experimental findings show the impossibility of extending *a priori* the results of Kaufman *et al.* to alloys having nitrogen concentrations above ~ 20 at. %. Indeed, below this concentration, the nitrogen substitution of carbon tends to maintain the planar geometry of graphite, producing a stressed and hard material.^{7,8} Above ~ 20 at. % nitrogen, the graphite sheets curl and a band of localized nitrogen lone pair is formed.⁹ The material

becomes less dense and $\text{-C}\equiv\text{N}$ species are promoted. Therefore, any study should take into consideration these structural differences.

In this work we analyze the influence of nitrogen and hydrogen on the vibration (ir and Raman spectra) properties of the carbon-nitrogen alloys with nitrogen concentration varying between 0–32 at. %. In the attempt to elucidate the origin of the ir absorption bands, samples deposited using the isotope $^{15}\text{N}_2$ and regular $^{14}\text{N}_2$ were grown in nominally identical conditions. To separate the influence of hydrogen and nitrogen, we have studied alloys with and without hydrogen, covering the range below and above 20-at. % nitrogen concentration. In a previous work, we have used D_2 to identify the existence of amines in the material.⁶ Those samples have been re-examined by focusing the attention in the 1000–1600 cm^{-1} region of the ir spectra, corresponding to vibrations associated with sp^2 bonds. In order to gain insight into the origin of the features observed in the spectra, we have performed calculations of the frequencies and intensities of the ir active vibrations of several organic molecules. These calculations are aimed at investigating the roles of symmetry-breaking effects of substitutional N in graphite structure and quantify the isotopic shifts due to ^{15}N . The theoretical vibration analysis is based on the quantum chemical Parametric Method 3 (PM3) technique.¹⁰ These calculations were carried out within the packages SPARTAN¹¹ and HYPERCHEM.¹²

II. EXPERIMENT

All the analyzed samples were obtained in a dual ion-beam-assisted-deposition system described elsewhere.⁵ A pure-graphite-carbon target (99.99%) was sputtered with Ar^+ ions of 1500 eV. Simultaneously, N_2^+ (H_2^+) ions species of ~ 100 eV were used to bombard the growing sample. The material was deposited on Si(111) and glass substrates. The nitrogen concentration was obtained *in situ* by electron x-ray photoemission spectroscopy. With this method concentrations differing in 1% can be distinguished.¹³ The thickness of the samples was measured using a profilometer. The shadow produced by the clip clamping the Si substrate to the sub-

strate holder formed a suitable step for the thickness measurement with an accuracy of $\sim 5\%$. In order to have comparable sample thicknesses (~ 5000 Å), suitable times of deposition were used. In particular, the growth rate of hydrogenated samples (20 Å/min) is half of that of nonhydrogenated samples. The ir and Raman spectra were obtained *ex situ* in a Fourier-transform infrared (FTIR) NICOLET 850 spectrometer and in a micro-Raman (excitation lines: 520.8 nm and 488 nm from Kr and Ar lasers), respectively. The ir spectra were obtained in the transmission mode of the spectrometer. A resolution of 4 cm^{-1} and ~ 2000 scans proved to be sufficient to obtain a good signal-to-noise ratio in the ir spectra. All the spectra were referred to a blank Si background substrate obtained from the same wafer used to deposit the films. The NICOLET spectrometer is permanently purged with dry nitrogen and the equipment is maintained in a room with controlled humidity (better than 48% relative humidity). The background of the Si blank substrate and the studied film spectra were obtained 30 min after loading the samples. This procedure proved to completely eliminate the vibration modes associated to atmospheric water and CO_2 . The main interest of this work resides in the variations introduced in the local structure by different concentrations of nitrogen and hydrogen in the alloys. Therefore, only normalized intensities are reported. The hydrogen (deuterium) concentrations were obtained by nuclear techniques. This technique usually provides an accuracy of $\sim 10\%$.⁶

III. THEORETICAL RESULTS

The theoretical approach relies on geometrical optimizations and vibrational analysis of carbon clusters suitably substituted by nitrogen atoms, as described below. These calculations are based upon the well known PM3 semiempirical technique. PM3 is derived from the Hartree-Fock theory combined with the linear combinations of atomic orbitals approach to the molecular orbitals. This method has been very successful in producing molecular conformations in agreement with experiment, as extensively documented in the literature. Though it has not been explicitly parametrized to do vibrational analysis, PM3 has been reported to give vibration frequencies in close agreement with more sophisticated theories.¹⁴ It is usual to adopt a compression factor in the range 0.85 – 0.95 to the calculated spectrum. The accuracy of ir intensities depends on the group of molecules considered. Several studies on aromatic hydrocarbons and nitrogen containing organic species have been carried out upon use of PM3 vibration spectra, with reasonable results,¹⁵ and at low computational cost compared to *ab initio* calculations. All simulated spectra were normalized for comparison purposes.

We start the study by analyzing the influence of symmetry on the ir and Raman spectra of small molecules (Fig. 1). Molecule *M1* is an aromatic molecular radical having D_{3h} symmetry. Substitution of the central carbon atom by N, as in molecule *M2*, is intended to investigate the effects due to charge rearrangement while in *M3* molecule the substitution site reduces the symmetry to C_{2v} . The molecular conformations were optimized and the vibration analysis was performed. A standard compression factor of 0.9 has been applied to correct the spectra. Figure 2 depicts the simulated

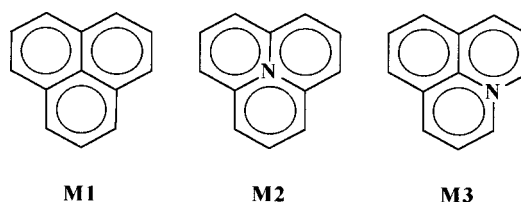


FIG. 1. Molecular models adopted in PM3 calculations of ir spectra.

spectra in the region 800 – 1600 cm^{-1} evaluated as Gaussian convolutions of the calculated intensities. The Gaussian line shapes were normalized to unity and weighted by the calculated PM3 intensities. The Gaussian broadening was arbitrarily taken as 20 cm^{-1} , a value smaller than the widening introduced by a combined effect of disorder and the apparatus resolution.

Molecule *M1* is very homogeneous in charge distribution and in C-C bond lengths, resulting in very low ir intensities in the stretching region, as expected. Notice that the curve in Fig. 2 corresponding to *M1* has been scaled by a factor of 10 to allow comparisons with the other spectra. Replacement of the central C atom by N brings a new charge distribution, in which second-neighbors carbons around N get negative charges through the π system. The consequence is the activation of C-C stretching vibrations, as seen in Fig. 2, in the region 1200 – 1600 cm^{-1} . These collective vibrations also include the C-N stretching, which shifts the spectrum to higher frequencies, from ~ 1500 to 1600 cm^{-1} . There are differences between the spectra of *M2* and *M3* due to their particular symmetry group, but the intensities are of the same order of magnitude. This means that the most relevant effect of N substitution in the ir spectrum of the aromatic system is the promotion of bond dipoles.

This result holds for larger systems provided that the aromaticity is preserved. We have performed similar calculations on large graphitic clusters containing up to 96 carbon atoms. Figure 3 depicts the simulated spectra for carbon clusters saturated with hydrogen at the end bonds, containing 6 and 26 nitrogen atoms randomly substituted, respectively. The plot corresponding to C_{96} has been scaled by a factor 10

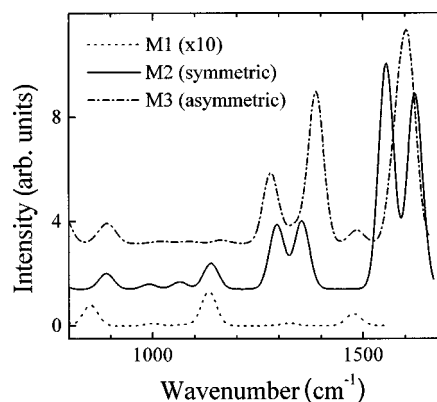


FIG. 2. Simulated PM3 ir-active vibration spectra (normalized intensities) of the model molecules *M1* (dotted line, scaled by 10), *M2* (solid line), and *M3* (dash-dotted line). The curves were translated upward for clarity.

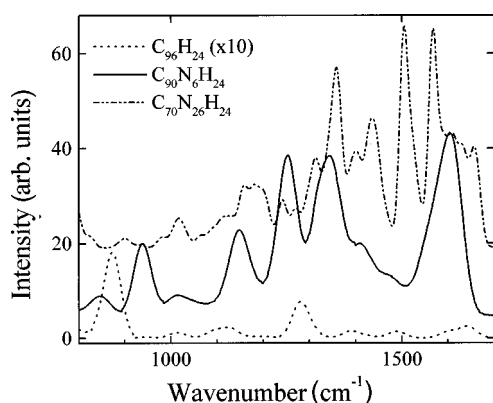


FIG. 3. Simulated ir spectra of large carbon clusters from PM3 calculations (normalized intensities). The curves were translated upward for clarity. $C_{96}H_{24}$ (dotted line, scaled by 10), $C_{90}N_6H_{24}$ (solid line), $C_{70}N_{26}H_{24}$ (dash-dotted line).

and successive plots are shifted upward for better visualization. These spectra show the same features seen in Fig. 2, namely, weak ir activity of the graphene cluster and the growing of structures in the range $1200\text{--}1600\text{ cm}^{-1}$ as nitrogen atoms are incorporated into the aromatic framework. These features are associated with collective C-C and C-N vibrations. The heavily doped cluster $C_{70}N_{26}H_{24}$ is not graphitic.⁹ In this disordered system the vibrations are localized in subclusters, giving rise to a more intricate spectrum. Indeed, the new frequencies appearing between $1400\text{--}1500\text{ cm}^{-1}$ are associated with the C=C skeletal bonds induced by the symmetry breaking introduced by N. As we will see below, this conclusion is confirmed by the negligible isotopic shift introduced by ^{15}N in this part of the ir spectra. Finally, the vibrations above 1600 cm^{-1} are due to the stretching of C=C bonds at the cluster edges.

Similar calculations were carried out to evaluate the isotopic effects of ^{15}N . We considered three situations: (1) simple systems such as the aromatic molecules *M2* and *M3* (Fig. 1), in which sp^2 hybridized N atoms participate in extended π electronic structure; (2) sp and sp^2 N atoms in $H_3C-C\equiv N$ and $H_3C-N=C(CH_3)_2$ structures; and (3) sp^3 N in large clusters like $C_{70}N_{26}H_{24}$. In aromatic systems the isotopic frequency shift is as small as 9 cm^{-1} , because the vibrations in which N atoms participate are collective, thus minimizing the effect of the isotope. The isotopic shifts of compounds formed by sp and sp^2 N are ~ 27 and 22 cm^{-1} , respectively. In the large cluster containing sp^3 N, several frequencies are shifted by an amount ranging from ~ 2 to $\sim 15\text{ cm}^{-1}$, but on average, the shift is below 10 cm^{-1} . The conclusion is that an effect of the ^{15}N isotope is clearly seen when the associated vibration is *localized*. For instance, $-C\equiv N$ species that appear in amorphous carbon-nitrogen alloys are expected to act as terminator groups and the associated vibrations are localized. In the case of $C\equiv N$, the calculated stretching vibration frequency shifts $\sim 30\text{ cm}^{-1}$ upon ^{15}N substitution. Therefore, in collective vibrations, the isotopic shifts will be rarely observed since other effects might produce similar modifications in the ir spectrum.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 4(a) represents the Raman and ir spectra of a *nonhydrogenated* sample containing 18 at. % nitrogen. The lack

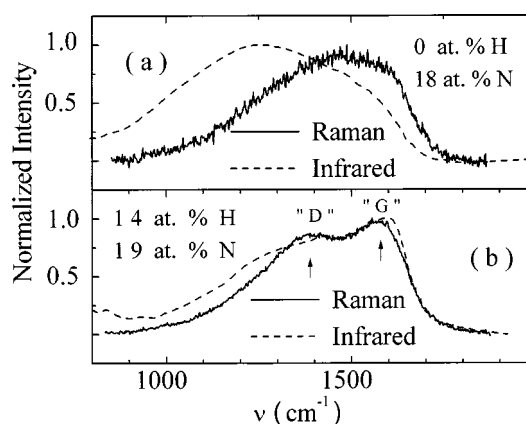


FIG. 4. Raman and ir spectra of *hydrogenated* and *nonhydrogenated* carbon nitride (only two of the studied samples are shown). Normalized intensities.

of coincidence of both curves shows that some vibration modes that are forbidden in Raman spectroscopy are allowed in ir spectroscopy and vice versa. This happens, for instance, in graphite, where the absence of bond dipoles makes the material ir inactive. On the other hand, since the transitions are allowed, graphite is Raman active.¹⁶ As remarked in the introduction, the similarities of the ir and Raman spectra obtained in *hydrogenated* carbon-nitrogen alloy was explained by Kaufman *et al.* by symmetry considerations.³ According to these investigators, nitrogen breaks the symmetry of the aromatic graphite rings making the material ir and Raman active. However, our results show a fairly good coincidence of the ir and Raman spectra in samples containing different quantities of hydrogen and constant N content, preventing to attribute exclusively to nitrogen the coincidence in these spectra [Fig. 4(b)]. For the sake of clarity, we have shown only the spectra for one sample but similar results are obtained for all the *hydrogenated* samples containing up to ~ 32 at. % nitrogen. Therefore, we remark that since Kaufman *et al.*³ studied *hydrogenated* samples, the ir spectra modifications observed by these authors probably stem from a combined effect of hydrogen and nitrogen inclusion in the alloy network. As observed in Fig. 4, the incorporation of hydrogen causes the increase of the intensity ratio $I(G)/I(D)$. Here, “G” identifies the band at $\sim 1570\text{ cm}^{-1}$ (“graphitic” component) and “D” the band at $\sim 1360\text{ cm}^{-1}$ (“disorder” component).¹⁶ Moreover, the intensity ratio $I(G)/I(D)$ is larger in *hydrogenated* samples when compared with *nonhydrogenated* samples. This result shows that hydrogen increases the ir activity of the aromatic graphitic rings forming the material. Another important result is that the spectra of the *hydrogenated* samples show much better defined bands than the *nonhydrogenated* samples [Figs. 4(b) and 5, inset]. This effect is observed in *diamonddike* materials (*a-C:H*) where the incorporation of hydrogen leads to the formation of smaller domains with molecular character.¹⁶ By comparison with this material, we suggest that hydrogen is acting as a terminator inducing the formation of a graphitic disordered network of domains with a molecular character. In *nonhydrogenated* samples the network is more interconnected, forming a compact material. Indeed, in a previous work we found that *hydrogenated* alloys are stress-free and less dense than *nonhydrogenated* materials.⁷ Furthermore, in

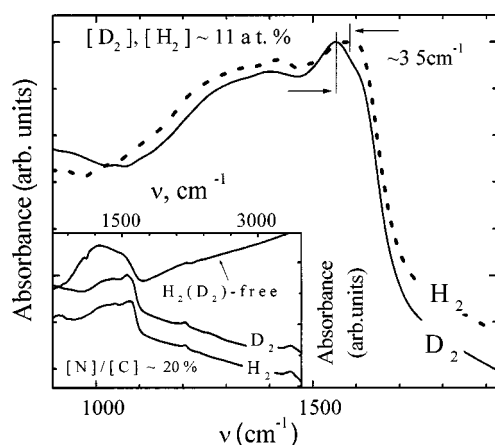


FIG. 5. Closeup of the hydrogenated and deuterated spectra. Inset: *nonhydrogenated*, hydrogenated, and deuterated infrared spectra. Normalized absorbances.

stressed materials, i.e., *nonhydrogenated*, the rigidity of the network probably imposes stringent selection rules, causing the differences observed between the Raman and ir spectra.

As remarked above, H₂ (D₂) substantially modified the spectrum of nitrogen-carbon samples (Fig. 5, inset). At first glance, Fig. 5 shows an apparent isotopic shift in deuterated samples, suggesting that hydrogen-containing complexes are contributing to vibration modes in the 1000–1600-cm⁻¹ region. In fact, we have studied several deuterated samples showing this type of trend which suggests a small isotopic shift. As discussed in the theoretical section, the simulated ir spectra depict vibration modes above 1600 cm⁻¹ due to the stretching of >C=C< bonds at the edges of the clusters. Indeed, the presence of hydrogen at the frontier of the cluster causes the rising of these structures (Fig. 3). Therefore, deuterium substitution will, in principle, affect this region of the spectrum.

There are, however, experimental limitations that prevent ascribing undoubtedly the peak shifts indicated in Fig. 5 to an isotopic effect. First, the ir difference spectra corresponding to deuterated and hydrogenated samples is as much as 10% of the original spectra areas. Second, as remarked above, the hydrogen (deuterium) concentrations are determined with an uncertainty of ~10% while variations in N concentration within 1% are also possible. Finally, in a previous work we have shown that hydrogenated samples, when exposed to the atmosphere, form hydroxyls association in extensive hydrogen-bond structures at ~3500 cm⁻¹, contributing to the discussed band.⁶ Therefore, although small changes could be present above 1600 cm⁻¹, the experiments of deuterium substitution are inconclusive. Therefore, these results suggest that the important variations in the ir activity observed below 1600 cm⁻¹ are *induced* by hydrogen in the skeletal structure formed by sp² bonds.

Figure 6 shows the normalized Raman (a) and ir (b) spectra of the studied *nonhydrogenated* samples. This plot shows some important features to be remarked: (1) only minor differences are found in the Raman spectra in all the studied samples despite the large nitrogen variations in the alloys; (2) although less dramatic than hydrogen, nitrogen also increases the *I(G)/I(D)* intensity ratio of the ir spectra; and (3) increasing the nitrogen content shifts the ir spectra to

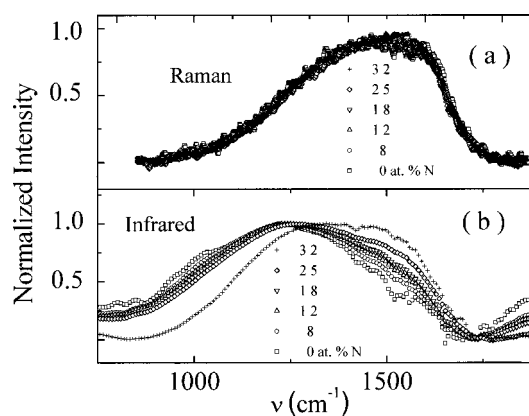


FIG. 6. Raman (a) and infrared (b) spectra of *nonhydrogenated* samples. Normalized intensities.

higher energies and the similitude of the ir and Raman spectra is evident.

As it was remarked above, Kaufman *et al.*³ have attributed the increasing ir activity on nitrogen incorporation to the symmetry breaking of aromatic and/or acetylene groups. This conclusion relies on the absence of isotopic effect in the ~1000–1600-cm⁻¹ region of the ir spectra by substitutional ¹⁵N in *hydrogenated* samples containing up to ~at. 20% nitrogen.³ In the attempt to separate the role of hydrogen in the results, we have studied the influence of ¹⁵N on the ir spectra of *nonhydrogenated* samples containing ~25–26-at. % nitrogen. This concentration was chosen because above ~20 at. % nitrogen content, profound changes occur in the material.^{7–9}

Figure 7 shows the ir spectra of two samples containing ¹⁴N (26±1) at. % and ¹⁵N (25±1) at. %. This spectra shows two well-differentiated bands at ~1000–1500 cm⁻¹ and at ~2150 cm⁻¹. The band associated with -C≡N (~2150 cm⁻¹) shifts Δω≈35 cm⁻¹, an amount consistent with the increased atomic mass and assuming a constant oscillator strength.³ This experimental shift agrees quite well with the ~30-cm⁻¹ theoretical shift obtained for -C≡N by the numerical analysis discussed above. Moreover, the difference spectra under the 2150-cm⁻¹ band is over 20% of the area of each individual band, a percentage that cannot be attributed

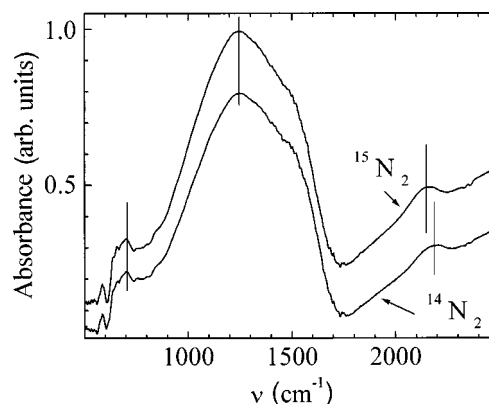


FIG. 7. Infrared spectra of the a-C¹⁵N_x and a-C¹⁴N_x samples with 25–26-at. % nitrogen content. For the sake of clarity, the curves are shifted by an arbitrary constant. Normalized intensities.

to experimental uncertainty. Therefore, we conclude that this shift is indeed produced by an isotopic effect.

The analysis of the main absorption band is more complicated. The numerical simulation shows that most of the features between 1000–1600 cm^{-1} are associated with C=C and C=N vibrations. It also shows that ^{15}N will not produce appreciable frequency shifts in this region of the ir spectrum. As in deuterated samples, the difference spectra of samples containing ^{15}N and ^{14}N is too small when compared with the area of the original bands. Furthermore, we have found that the spectra of two samples containing (26 ± 1) at. % and (24 ± 1) at. % of ^{14}N , respectively, can account for this difference spectra. Therefore, the lack of a clear isotopic shift strongly suggests that nitrogen is bonded in large clusters rather than in isolated bonds, as supported by the numerical calculations.

V. SUMMARY AND CONCLUSIONS

We summarize the above findings as follows.

(1) The Raman and the ir spectra of *nonhydrogenated* samples are different in films containing up to ~ 20 -at. % nitrogen concentration. The numerical simulations show that, in *nonhydrogenated* films containing up to ~ 20 -at. % nitrogen, the increasing activity of the ir spectra is due to the promotion of bond dipoles by N substitution in graphene aromatic systems. Above this concentration two sources contribute to the increasing ir activity: (a) as before, dipole promotion, and (b) the bending and curling of the aromatic rings, introduced by the incorporation of nitrogen, break the

symmetry of the system, inducing stronger localized vibrations in the 1300–1600- cm^{-1} region of the ir spectra.^{7–9} The stress reduction introduced by nitrogen imposes less stringent selection rules and, consequently, quite similar Raman and ir spectra are obtained.

(2) Numerical simulations show that ^{15}N substitution in large clusters does not produce significant shifts in the main ir absorption band (~ 1000 – 1600 cm^{-1}). The absence of isotopic shift in nonhydrogenated material containing ~ 25 – 26 -at. % ^{15}N strongly suggests that nitrogen is mostly incorporated in large clusters.

(3) Hydrogen incorporation (maintaining constant nitrogen concentration) produces the same effect as nitrogen just described in (1) though the changes are stronger. Indeed, the incorporation of a relatively small amount of hydrogen increases their activity of the aromatic rings that are assumed to form the material. As a consequence, a fairly good similitude of the ir and Raman spectra is obtained. The ir spectra of deuterated samples show that hydrogen is not directly involved in the strong activity observed around 1000–1600 cm^{-1} .

ACKNOWLEDGMENTS

The authors are indebted to D. Comedi for reading the manuscript, to F. Ikawa, R. G. Lacerda, and R. Zannata for the Raman and ir measurements, and to I. Baunvold for kindly providing the $^{15}\text{N}_2$ gas. This work was partially supported by FAPESP and CNPq. N.M.V., M.C.d.S., and F.A. acknowledge financial support from CNPq.

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