Polyamines Adsorbed onto Silica Gel: A Raman Microprobe Analysis

E. GAILLIEZ-DEGREMONT,[1] M. BACQUET,[1] J. LAUREYNS,[2] M. MORCELLET[1]

[1] Laboratoire de Chimie Macromoléculaire URA-CNRS 351, USTL, 59655 Villeneuve d'Ascq Cedex, France

[2] Laboratoire de Spectroscopie Infrarouge et Raman UPA-CNRS 2631, USTL, 59655 Villeneuve d'Ascq Cedex, France

ABSTRACT: Polyamine [especially poly(ethylenimine) and poly(4-vinylpyridine)] adsorption onto silica gels for chromatography and water-decontamination experiments, using a Raman microprobe, is reviewed. First, the bare silica are characterized. Then, the polyamines and the adsorbed polyamines spectra are compared. We show that polyamine adsorption onto silica occurs with two kinds of polymer populations: chemisorbed (trains due to important interactions between silanol and the nitrogen atom) and physisorbed (multilayers) polymer. The modifications of chemisorbed polymer bands are stronger than are the physisorbed ones. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 871–882, 1997

INTRODUCTION

Porous silica gels are usual supports for high-performance liquid chromatography.[1,2] These supports, often called packings, are generally modified by coated or chemically bound polymer.[3] In the literature, the thickness of the coated polymer layer is often described in terms of trains, loops, and tails.[4]

In our laboratory, we developed water-decontamination applications with these coated silica gels. Some pollutants were found to be successfully eliminated from water by polyamine-coated silica beads. A detailed study of heavy metal adsorption onto coated silica is in progress.[5] A better understanding of polymer/silica interactions would allow us to correlate results of decontamination experiments (pollutant removing) with the support structure.

The aim of this work was to study in much detail the adsorption of polyamines [especially poly(4-vinylpyridine) and polyethylenimine] onto silica gel using a Raman microprobe. In a previous article, textural aspects of bare silica were accurately described. Due to optical and scanning electron microscopies and X-ray microanalysis, we have a good knowledge of silica surfaces and textures.[6] Bare silica presents textural and chemical heterogeneities, which govern polymer adsorption. The adsorption is more efficient when the specific area is high and the bead structure is more compact.

In this article, the bare silica packings are first characterized. Then, the polymer and the adsorbed polymer spectra are compared to try to explain how the polymer adsorbs. We try to display the polyamine chemical functions involved into the adsorption process. Finally, we will be able to improve and optimize the P4VP and the PEI/silica systems used as adsorbents.

EXPERIMENTAL

Materials

Two spherical porous silica gels (Nucleosil, from Macherey Nägel) were used as supports for the preparation of coatings. Their characteristics are

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Correspondence to: M. Morcellet.

Table I Characteristics of Bare Packings

Sample Designation	R_p (Å) com.	R_p (Å) meas.	S (m²/g) com.	S (m²/g) meas.	Size (μm) com.	Size (μm) meas.	V_p (Cm³/g) com.	V_p (Cm³/g) meas.
Nu100-30	100	67	350	303	30 (25–40)	25 (9–43)	1	1
Nu1000-30	1000	943	25	43	30 (25–40)	27 (9–43)	0.8	0.9

com: given from the supplier; meas: measured; R_p: pore mean radius; S: specific surface; size: silica beads mean diameter; V_p: porous volume.

summarized in Table I. A specific area was determined using BET isotherms (Apparatus Quantasorb Junior) by nitrogen adsorption and measurements. For Nu100-30, the porous volume and distribution was realized using BJH isotherms, with the same apparatus. As the BJH method for porous volume is limited to 300 Å porosity, the porous volume and distribution were determined using mercury porosimetry for Nu1000-30. The size repartition of the beads was achieved by optical microscopy, with a sampling of 1500 beads.

The two polymers used for the sorption were

1. *Polyethylenimine* (PEI): This commercial branched polymer (Aldrich), in solution in water, was freeze-dried. Its average molecular weight (M_w) is 750,000 g/mol. It contains primary, secondary, and tertiary amino groups in a ratio of approximately 25, 50, and 25%, respectively.

2. *Poly(4-vinylpyridine)* (P4VP): This was synthesized by radical solution polymerization in methanol, then precipitated in ethyl ether. Its average molecular weight (M_v), determined by capillary viscosimetry using the Mark–Houwink relation, is 64,000 g/mol.[7]

These polymers were adsorbed onto silica by a procedure already described.[8] The concentrations of the coating solutions used to study the influence of the adsorbed polymer amount were 0.5 and 5% in weight of polymer in methanol. The quantities of polymer adsorbed were obtained from elemental analysis (Microanalysis Service CNRS, Vernai-

Table II Textural and Chemical Characteristics of Coated Packings

	Silica					
	Nu100-30	Nu100-30	Nu1000-30	Nu100-30	Nu100-30	Nu1000-30
	Polymer					
	P4VP	P4VP	P4VP	PEI	PEI	PEI
	Concn. (% w/v)					
	5	0.5	5	5	0.5	5
	Designation					
	Nu100/P4VP5%	Nu100/P4VP0.5%	Nu1000/P4VP5%	Nu100/PEI5%	Nu100/PEI0.5%	Nu1000/PEI5%
S (m²/g)	217	261	40.5	186	242	35
R_P (Å)	64		779	60		664
Coat. poly.	153.5	68.5	40.5	149.5	36.5	38
A_s (mg/m²)	0.7	0.2	1	0.8	0.1	1.1

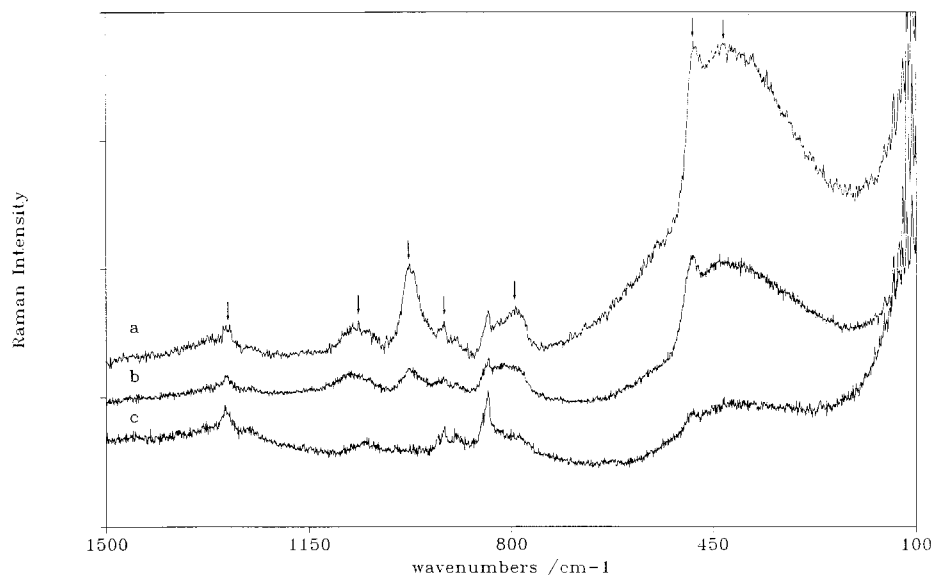Coat. poly.: polymer coated (mg) for 1 g of coated silica. A_s: Coat. poly./S.

Figure 1 Raman spectra of bare silica: (a) Nu100-30; (b) transparent Nu1000-30; (c) colored Nu1000-30.

son). The chemical and physical characteristics of the coated silica beads are listed in Table II.

Raman Microprobe Analysis

Local molecular analysis was carried out using a multichannel Raman spectrometer (DILOR XY) equipped with a CCD detector. The band positions were accurate to ± 1 cm^{-1}. Data were typically obtained with a laser excitation wavelength of 514.5 nm. All spectra were taken at 20–40 mW on the sample, except for P4VP (4–10 mW) to avoid any degradation, using a 100× Olympus objective (N.A. 0.95). Lateral spatial resolution was

about 1–2 μm. The polymers and the silica beads were just put onto a glass slide. Dry and moist states of the samples were studied. Several experiments were done on the same bead and on different beads of a given sample to obtain significant information.

RESULTS AND DISCUSSION

Bare Silica

According to Table I, larger size and porosity repartitions than the commercial values were found

Table III Tentative Assignment of Bands Found in Laser Raman Spectrum of Bare Silica

Wavenumber (cm^{-1})	Intensity	Assignment
430–440	s	In-plane Si—O—Si
490–495	s	Silica D_1 defect
800	m	Si—O—Si symmetric stretching and Si—C stretching
1070	w	Si—O—Si asymmetric stretching
842	m	Additional band from objective
910–920	w	Surface silanols stretching
970–980	m	Surface and internal silanols stretching
1300	w	Si(CH$_3$) symmetric deformation No band detected until 3700 cm^{-1}

s = strong; m = medium; w = weak.

for Nu100 and Nu1000-30 beads. As expressed in our previous article, these beads consist of agglomerates of 0.1–0.5 μm particles, called elementary particules.[6]

But, especially for Nu1000, heterogeneities in porosity appear, due to differences in the fitting of these particules. The heterogeneous texture is associated with the different bead colors when they are observed under optical microscopy. There are transparent beads (in transmission) for which the fitting is compact (Nu100-30 and some Nu1000-30). Also, there are colored and black ones (the others Nu1000-30) for which the fitting is rather loose. The black beads have pores greater than 2000 Å. A preliminary study on a Raman spectrometer also showed that all the transparent beads present the same spectrum. This one is characterized by a broad band between 250 and 500 cm^{-1} attributed to the in-plane Si—-O—Si bending. The colored and black beads offer the same spectrum but with a noisy signal, because of a partial loss of the light intensity due to the diffusion process.

In this work, a detailed Raman study using a CCD detector is presented, giving more resolved spectra (Fig. 1). Assignments of the main silica bands are summarized in Table III.

The broad band between 200 and 500 cm^{-1} can be decomposed into two bands:

1. The 430–440 cm^{-1} band is the more intense band of the vitreous silica.[9] It is characteristic of the silica tetrahedra three-dimensional network.

2. The 490–495 cm^{-1} band is called the D_1 defect. In the literature, two Raman silica bands for 490 and 605 cm^{-1} are observed for high surface area and vitreous samples.[10,11] These two bands are usually ascribed to D_1 and D_2 silica defects. Their attribution is very controversial. The D_1 band is generally assigned to a vibrational mode of [SiO$_4$] tetrahedra with a nonbridging oxygen atom, i.e., the oxygen atom bonded to one silicium atom [Fig. 2(a)]. This band is more intense for the transparent beads, these having the higher specific surface.

The structure of silica giving D_2 is related to the surface condensation (between 200 and 500°C) of weakly interacting silanols. The different silanols are presented in Figure 2(b): free and bonded silanols, vicinal, and hydrated silanols. Thus, D_2
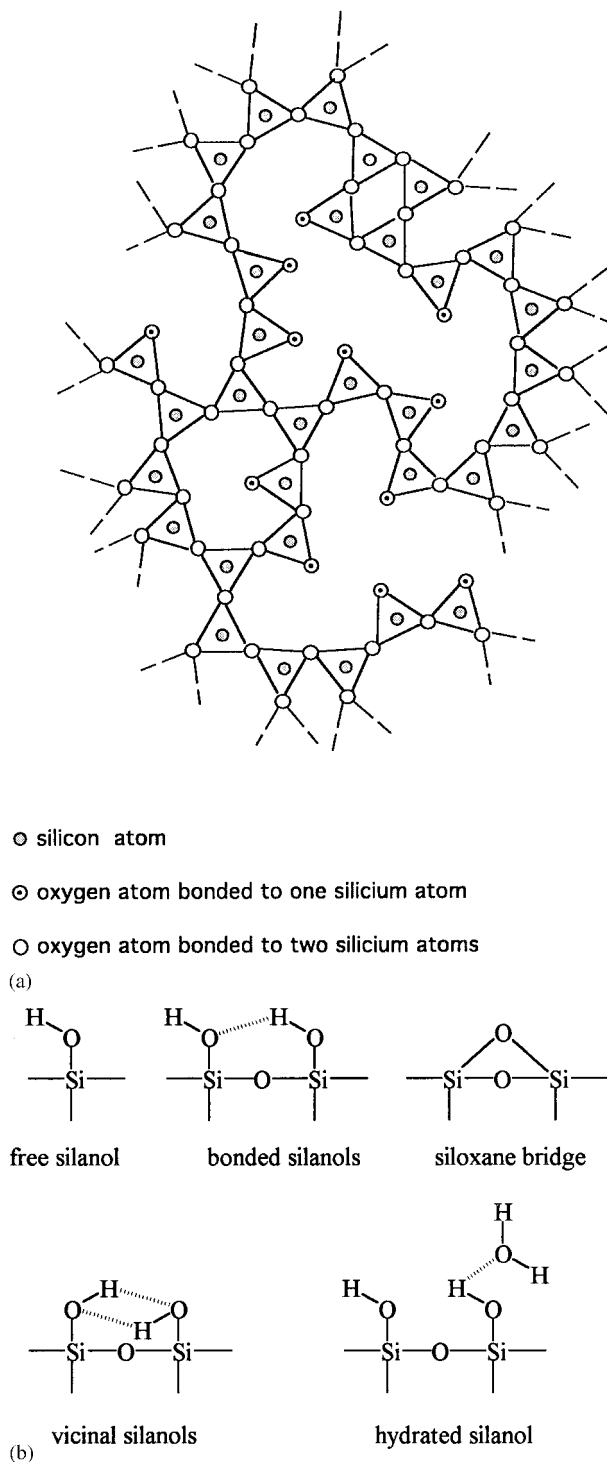

o silicon atom

⊙ oxygen atom bonded to one silicium atom

○ oxygen atom bonded to two silicium atoms

(a)

(b)

Figure 2 Silica framework, silanols, and siloxane bridges: (a) silica framework: bridging and nonbridging oxygens; (b) silanols and siloxane bridges.

appears only for a thermally treated silica.[12] D_1 appears in the chromatographic silica gel[13] and for other vitreous silicas spectra.[14] Nu100 and
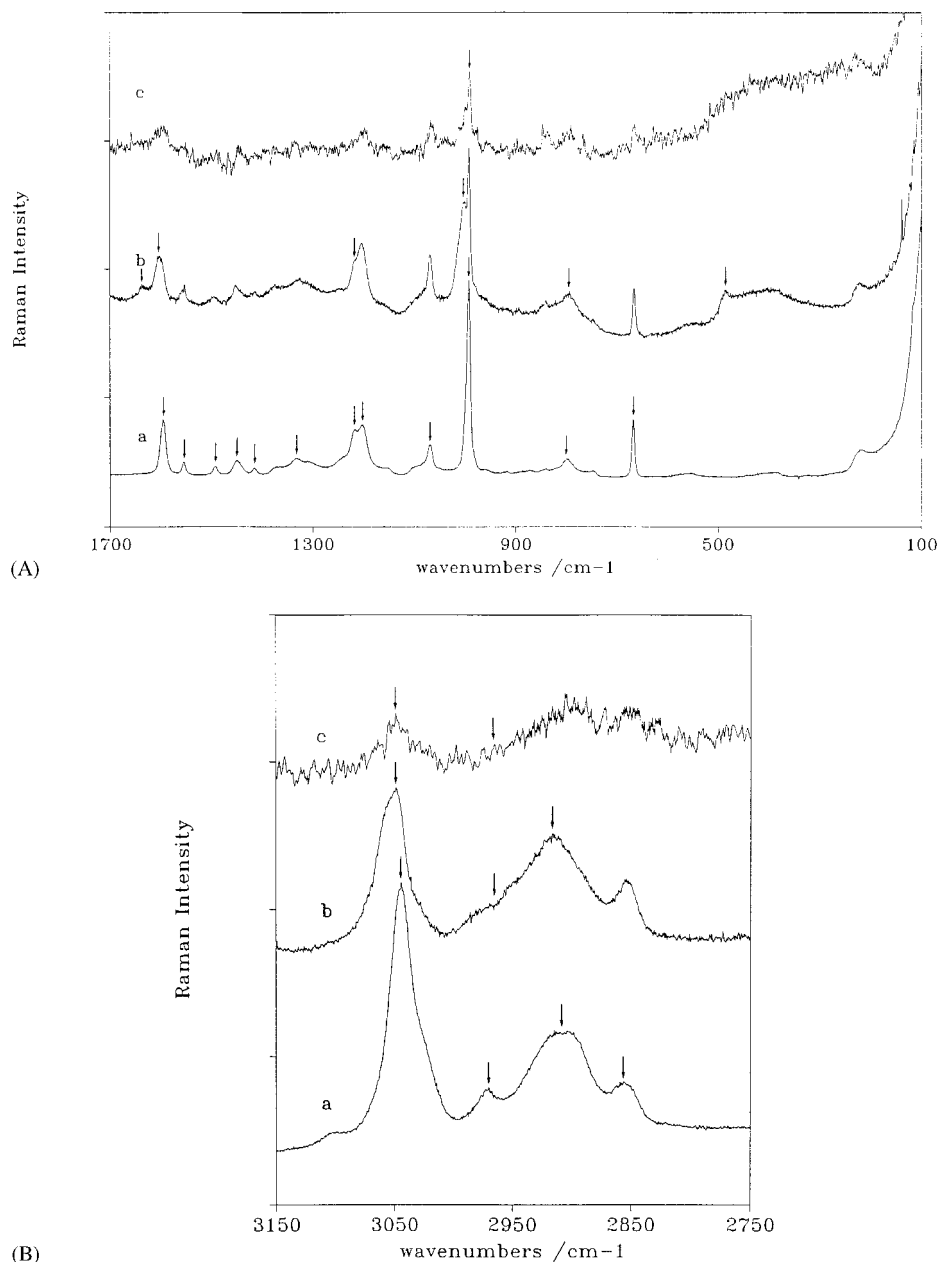
(A)

(B)

Figure 3 Influence of texture on Raman spectra of P4VP-coated silica. (A) The [100–1700] spectrum region; (B) the [2750–3150] spectrum region: (a) P4VP; (b) P4VP-coated transparent bead (Nu100/P4VP5% and some Nu1000/P4VP5%); (c) P4VP-coated colored bead (Nu1000/P4VP5%).

Nu1000-30 do not present D_2 because of their hydroxylate surfaces (there are many hydrated silanols).

We note differences among the transparent beads (between the Nu100-30 [Fig. 1(a)] and the Nu1000-30 [Fig. 1(b)]. For the Nu100-30 beads, the 970–980 cm^{-1} band is strong and there is an additional one (910–920 cm^{-1}). These two bands

are typical of silanols. There are more silanols onto the Nu100-30 because of its large specific surface. The 970–980 cm^{-1} one completely disappears for the black Nu1000-30 beads [Fig. 1(c)]. Because of the large porosity, there are not enough silanols on the surface to be detected. For all the beads, we also note silica polymerization wastes due to alkylsilicate monomer residues: The

Table IV Tentative Assignment of Bands Found in Laser Raman Spectrum of P4VP

Wavenumber (cm^{-1})	Intensity	Assignment
666	m	Out-of-plane ring vibration
800	w	Two adjacent H ring out-of-plane vibration
842	m	Additional band from objective
993	s	Ring breathing
1068	m	Ring bending
1202	m	In-plane H ring bending
1218	m	In-plane H ring bending
1333	w	
1413	w	Aliphatic CH_2 and CH deformations (waggings)
1450	w	
1492	w	Ring stretching
1553	w	Ring stretching
1596	m	C=N ring stretching
2855	m	aliphatic CH_2 symmetric stretching
2909	s	Aliphatic CH_2 asymmetric stretching, aliphatic asymmetric CH stretching
2970	m	CH symmetric ring stretching
3044	s	CH asymmetric ring stretching

s = strong; m = medium; w = weak.

1300 cm^{-1} band is typical of $Si(CH_3)$ deformation and a part of the 800 cm^{-1} one corresponds to Si—C stretching.

Coated Silica

Textural and chemical characteristics of P4VP- and PEI-coated beads are presented in Table II. For the coated beads, the porous volume and specific surface globally decrease. For the coated Nu100-30 (with 5% polymer concentration), the adsorbed polymer amount, in mg for 1 g of coated silica, is greater than for Nu1000-30 (5%). But it becomes more important for the Nu1000-30 when it is expressed in mg for 1 m^2 of coated silica. When the polymer concentration is 0.5%, the adsorbed polymer amount in mg/m^2 decreases, especially for Nu100-30/PEI0.5%.

P4VP-coated Silica

The P4VP spectrum is given in Figure 3(A) and (B,a). Attribution of P4VP bands was performed by comparison between polystyrene and pyridine literature spectra[15–17] and our ethylpyridine spec-

trum. Assignments of P4VP bands are summarized in Table IV.

Raman observations of P4VP-coated silica reveal that the more the bead is colored (with a split structure) the less it adsorbs. For transparent beads (with a compact structure), the P4VP-adsorbed spectrum is more detailed and resolved.

The [100–1700 cm^{-1}] Spectrum Region. The transparent Nu100 and Nu1000/P4VP5% beads present the typical silica broad band between 430–490 cm^{-1} and we notice some modifications of the P4VP adsorbed [Fig. 3(A,b)]. We note the broadening of the 800 cm^{-1} band, because of the superposition of the silica contributions and the P4VP band. The in-plane H ring bending bands (1202 and 1218 cm^{-1}) have a different shape; the 1218 cm^{-1} band seems to decrease. The 1596 one is characteristic of aromatic P4VP ring shifts from about 5 cm^{-1} and presents an additional shoulder (1630 cm^{-1}).

One of the most important spectrum modifications is the 993 cm^{-1} P4VP band. This one broadens, and a second one (1002 cm^{-1}) appears. This second band is probably due to the pyridine ring binding by hydrogen bonds to a surface OH group
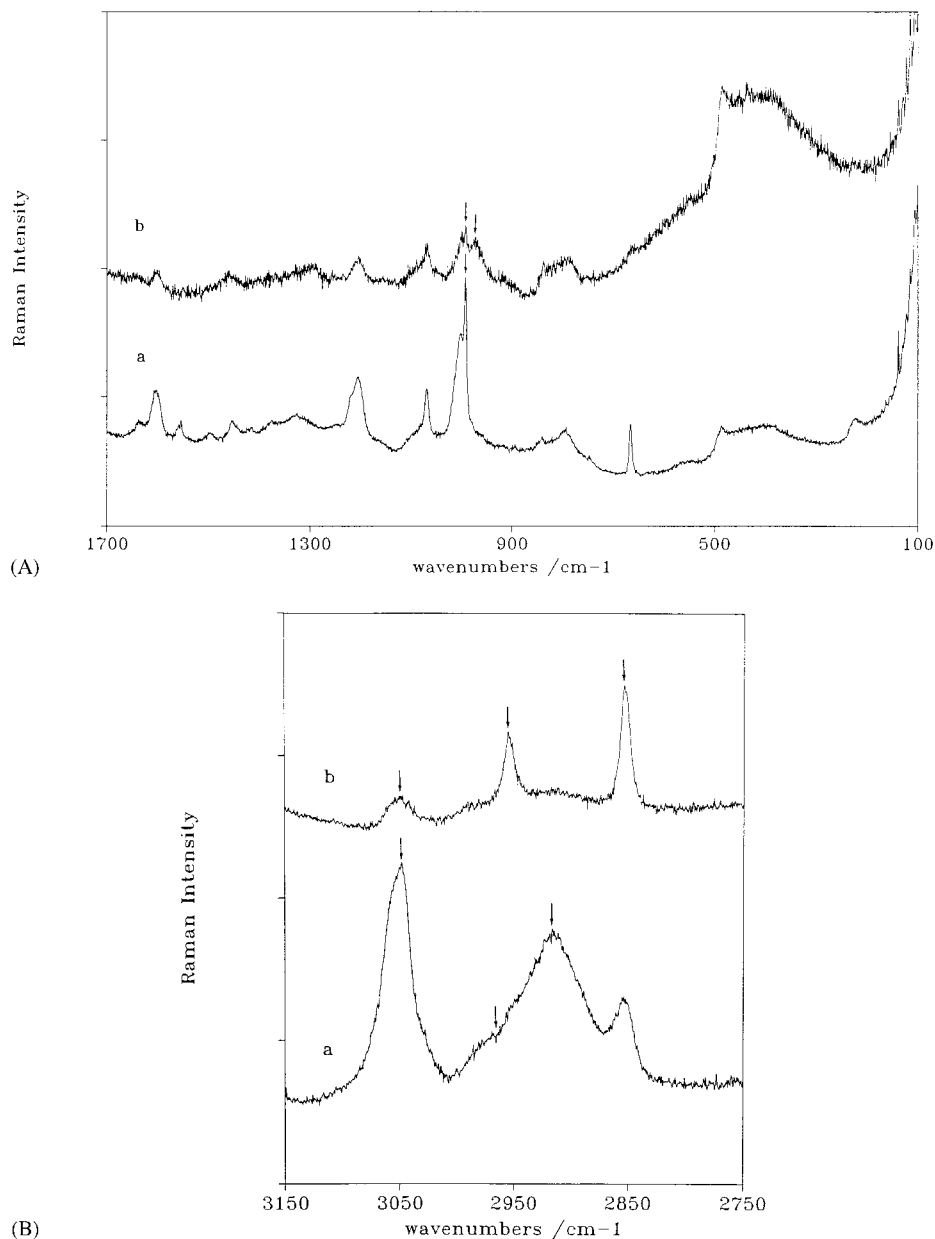
Figure 4 Influence of quantity on Raman spectra of P4VP-coated silica. (A) The [100–1700] spectrum region; (B) the [2750–3150] spectrum region: (a) P4VP-coated transparent bead (Nu100/P4VP5%); (b) P4VP-coated transparent bead (Nu100/P4VP0,5%).

(silanol).[18] In a work on pyridine adsorbed onto silica, Hendra et al. showed that the pyridine Raman spectrum changes as the pyridine is desorbed from silica.[19] At high coverage, the ring breathing band (989 cm^{-1} for pyridine) is present due to bulk physisorbed pyridine. At medium coverage, a second band appears (1004 cm^{-1}), showing the presence of hydrogen-bonded pyridine (with the silica surface silanols). At weak coverage, only

the 1004 cm^{-1} band remains. Thus, this study confirms the two kinds of P4VP populations adsorbed onto the transparent beads: P4VP chemically adsorbed by ring/silica interactions and P4VP physically adsorbed due to multilayers or loops and tails.

To evaluate the influence of the amount of adsorbed polymer, the Nu100/P4VP0.5% (corresponding to the half of the maximum amount of
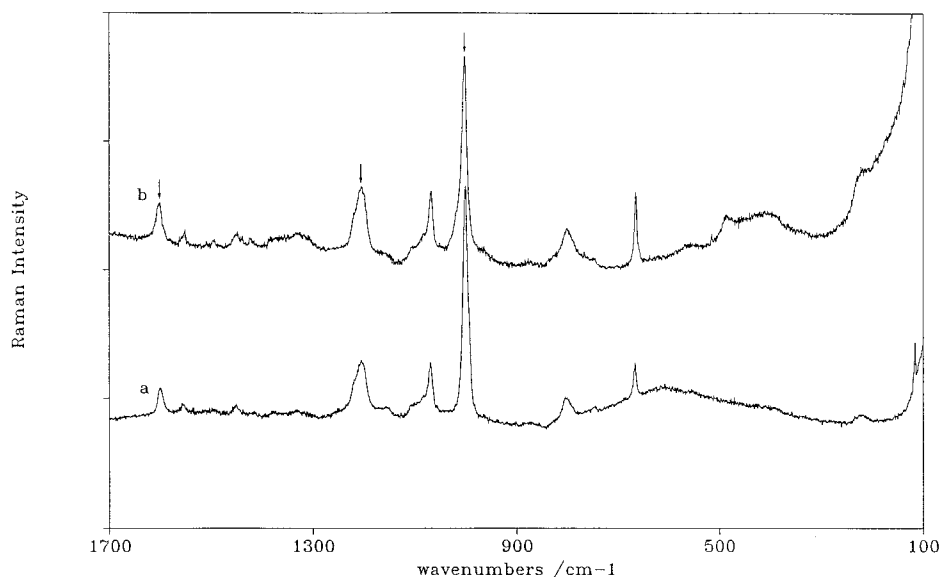
Figure 5 Influence of moistness on Raman spectra of P4VP-coated silica: (a) P4VP immersed in water; (b) P4VP-coated transparent bead (Nu100/P4VP5%), immersed in water.

polymer adsorbed) and the Nu100/P4VP5% spectra were compared [Fig. 4(A,a,b)]. We recognize some polymer bands, even if they are very weak. Among the silica bands, the typical silanol stretching band (970–980 cm^{-1}) appears. This one does not exist for Nu100/P4VP5%. This means that when the polymer adsorbed amount decreases, free silanols appear. The broadening and split of the band at 992 cm^{-1} are not obvious for Nu100/P4VP0.5%.

The colored Nu1000/P4VP5% beads offer a noisy and weak signal [Fig. 3(A,c)]. The polymer adsorption is not very efficient when the structure is loose. We identify some polymer bands, but we note the same weak intensity for the silica and polymer bands. The 993 cm^{-1} band seems to split.

Our supports are used in a water medium for decontamination experiments. So, it is interesting to identify the polymer/silica interface in moist medium. Fortunately, water is transparent in our wavelength-range Raman study. The spectra of P4VP and the transparent coated bead immersed in distilled water are given in Figure 5(a) and (b). On the one hand, the water-immersed P4VP spectrum presents some differences compared to the "dry" P4VP spectrum. The 993 and 1595 cm^{-1} bands shift to 1001 and 1601 cm^{-1}, respectively. Also, the in-plane H ring bending bands present a different shape: The 1218 cm^{-1} one seems to disappear. On the other hand, the water-immersed coated bead spectrum is very similar to

the water-immersed P4VP spectrum. Only the 1001 cm^{-1} band remains, being modified by weak broadening.

We have supposed that there are two kinds of P4VP populations adsorbed onto the transparent beads. Then, the 1001 cm^{-1} band for the water-immersed coated bead may correspond to two hydrogen-bonding contributions: between pyridine and silanols and between bulk physisorbed polymer and water. Water makes hydrogen bondings with P4VP loops and tails, and this contribution is predominant in the spectrum. So, the directly adsorbed P4VP amount onto silica by hydrogen bondings is not very important. For water-decontamination applications, the P4VP loops and tails will be efficient.

The [2750–3150 cm^{-1}] Spectrum Region. This region also presents important modifications. These concern the CH pyridine and CH$_2$ and CH skeleton polymer characteristic bands [Fig. 3(B)].

First, we consider the CH pyridine ring stretchings: For the transparent beads, the two bands are modified [Fig. 3(B,b)]. The 3044 cm^{-1} band is shifted and the 2970 cm^{-1} one completely disappears. We notice the same modifications for the Nu100/P4VP0.5% spectrum [Fig. 4(B,b)] and the noisy one of the colored beads [Fig. 3(B,c)]. Thus, the polymer adsorption modifies the CH ring symmetric stretching and prevents the CH ring asymmetric one. There are probably specific interac-
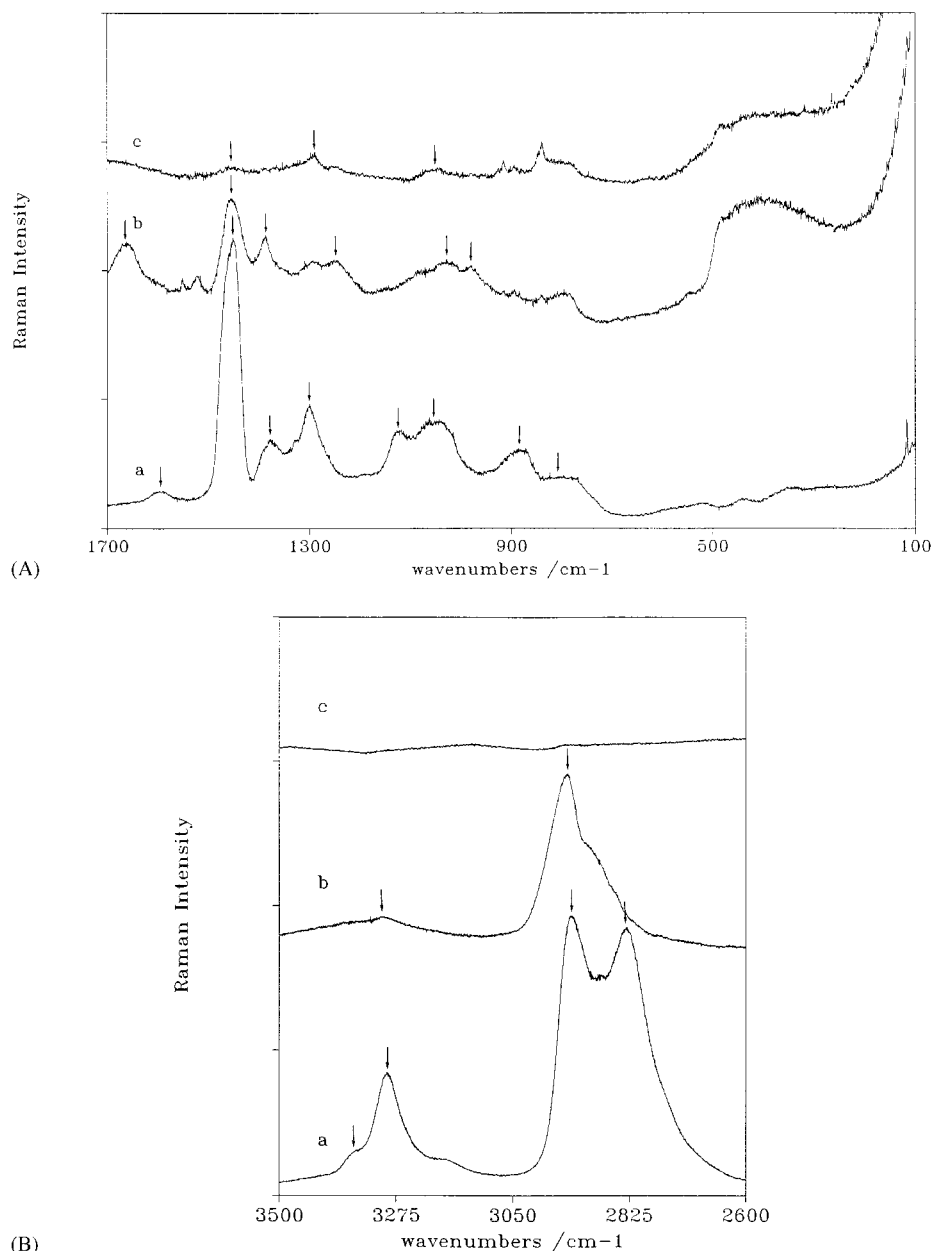
(A)

(B)

Figure 6 Influence of texture on Raman spectra of PEI-coated silica. (A) The [100–1700] spectrum region; (B) the [2600–3500] spectrum region: (a) PEI; (b) PEI-coated transparent bead (Nu100/PEI5% and some Nu1000/PEI5%); (c) PEI-coated colored bead (Nu1000/PEI5%).

tions, different from the hydrogen bonding between P4VP and silica.

Second, one of the polymer skeleton bands is modified. For the transparent beads Nu100/P4VP5%, the 2909 cm^{-1} band is shifted. But this band totally disappears and is replaced by a strong band at 2955 cm^{-1} for the Nu100/P4VP0.5% transparent beads [Fig. 4(b)]. Thus,

polymer adsorption modifies the polymer skeleton.

For this region, the skeleton and pyridine ring band modifications are more important for a small amount of polymer adsorbed. This is may be indicative of the two polymer populations. When the amount of polymer adsorbed increases, there is more bulk physisorbed polymer, which masks the

Table V   Tentative Assignment of Bands Found in Laser Raman Spectrum of PEI

Wavenumber (cm^{-1})	Intensity	Assignment
800	w	NH_2 deformation (wagging)
885	m	NH_2 deformation (wagging)
842	m	Additional band from objective
1046	m	C—N stretching (Ist and IInd amines)
1120	m	C—N stretching (IIst amines)
1300	m	
1378	m	Aliphatic CH_2 deformations (waggings)
1449	s	
1600	w	NH_2 deformation
2855	vs	CH_2 symmetric stretching
2938	vs	CH_2 asymmetric stretching
3292	s	NH_2 symmetric stretching
3360	w	NH_2 asymmetric stretching

vs = very strong; s = strong; m = medium; w = weak.

modifications due to the chemically adsorbed polymer.

PEI-coated Beads

There is no Raman study of PEI in the literature. So, band attributions [Fig. 6(A) and (B,a) and Table V] were achieved with reference to n-propylamine and di-n-butylamine spectra acquisitions, to distinguish Ist and IInd amine functions.[20,21]

The 100–1700 cm^{-1} Spectrum Region. For coated beads, PEI bands are less intense than are P4VP bands compared to silica bands. As for P4VP-coated beads, Figure 6 shows that the darker the bead, the less it adsorbs the polymer. In the case of transparent beads [Nu100/PEI5% and some Nu1000/PEI5%, Fig. 6(A,b)], we recognize some characteristic silica bands. For the transparent Nu100/PEI5%, we note the emergence of the 980 cm^{-1} band, typical of silanols.

The adsorbed polymer spectrum presents many modifications. The C—N stretching bands for the Ist and IInd amines seem to disappear (1046 and 1120 cm^{-1}). Instead, we note the emergence of a weak band near 1030 cm^{-1}. The 1600 cm^{-1} one, characteristic of the NH_2 deformations, seems to be exalted because of the adsorption process: It strongly increases, broadens, and shifts. The 885 cm^{-1} one disappears.

All the bands typical of the primary and secondary amine functions in the polymer chain are changed. This is characteristic of specific interactions between PEI amine functions and silica. But, unlike P4VP, we note the emergence of the surface silanol band. It is surprising, because we could expect a better chemical interaction between silanols and NH or NH_2 groups than between silanols and N=C in a pyridine ring. This phenomen may be explained by the branched skeleton of the PEI compared to the linear skeleton of the P4VP.

In the case of colored beads, the spectrum is very weak [Fig. 6(A,c)]. Polymer band intensity decreases or these bands completely disappear. For instance, there are no more NH_2 and NH bands. We find the same characteristics for the Nu100/PEI0.5% beads [Fig. 7(A,b)]. These present almost the same amount of the adsorbed polymer (in mg/g) as for Nu1000 but not the same structure. We recognize the silica bands, especially the silanol band at 970–980 cm^{-1}, which is relatively more intense than for Nu100/PEI5%. That means that as for the Nu100/PEI5% the PEI does not overlay all the silica surface area.

The other important alteration concerns the skeleton methylene bands. The spectrum region between 1200 and 1500 cm^{-1} for transparent Nu100 and Nu1000/PEI5% beads is fully modified. The most intense polymer band, typical of
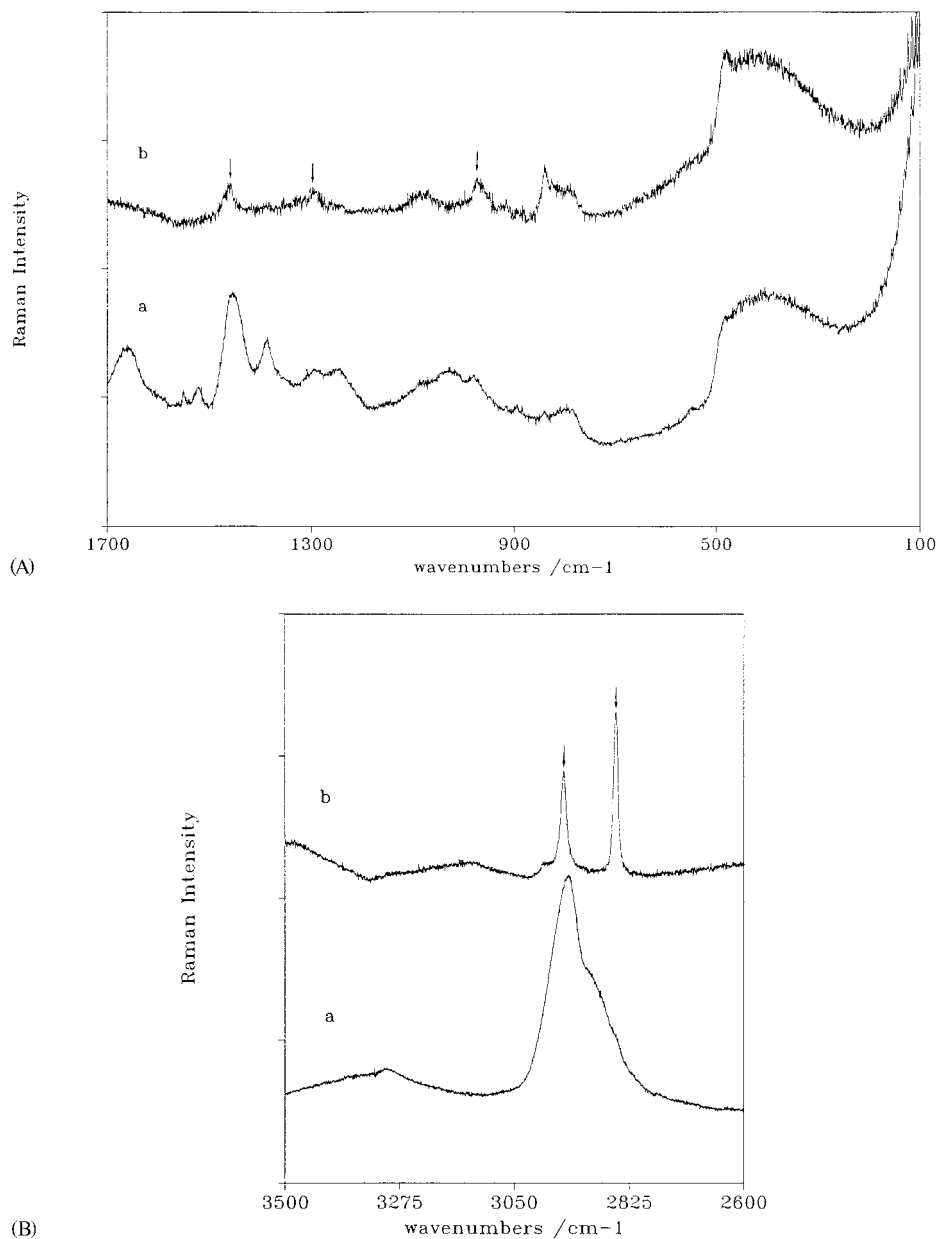
Figure 7 Influence of quantity on Raman spectra of PEI-coated silica. (A) The [100–1700] spectrum region; (B) the [2600–3500] spectrum region; (a) PEI-coated transparent bead (Nu100/PEI5%); (b) PEI-coated transparent bead (Nu100/PEI0.5%).

CH_2 and CH deformations (1449 cm^{-1}), decreases, whereas the 1378 cm^{-1} one increases. The 1300 cm^{-1} band shifts and broadens. For the colored Nu1000/PEI5% and transparent Nu100/PEI0.5% beads, we note only weak bands near 1250 and 1449 cm^{-1}.

The 2600–3500 Spectrum Region. For PEI-coated silica, the 3292 cm^{-1} band (corresponding to NH_2 stretching) intensity strongly decreases [Fig. 6(B)]. The aliphatic CH_2 and CH stretching bands are very modified. For the transparent Nu100 and Nu1000/PEI5% beads also [Fig. 6(B,b)], the antisymmetric band is shifted. The symmetric one has completely disappeared. We obtain only one large antisymmetric band. Thus, polymer adsorption onto silica in the case of PEI also modifies the polymer skeleton. For the Nu100/PEI0.5% beads [Fig. 7(B,b)], the spectrum region centered on 3000 cm^{-1} is more altered. In this case, the aliphatic carbon bands are

both shifted. They become finer and are quite opened out.

As for P4VP, the skeleton band broadening is characteristic of PEI multilayers (loops and tails) onto the bead. The spectrum modifications due to polymer skeleton are more important for a small polymer adsorbed amount onto a compact bead (with a large specific surface).

CONCLUSION

In this Raman study, two bare silica types were studied: Nu100 and Nu1000. Nu100 presents more silanols than does Nu1000. These two silica were coated with two polyamines: P4VP and PEI. In the case of P4VP coating, silanols are fully "passived." But with PEI, free silanols still exist.

We have shown that P4VP and PEI adsorption onto silica occurs with two kinds of polymer populations: chemisorbed and physisorbed polymers. The modifications in the chemisorbed polymer bands are strong compared to the physisorbed polymer ones. When the polymer is directly adsorbed onto the surface (trains), important interactions between silanol and nitrogen atoms (in the pyridine ring for P4VP, and NH and NH_2 amine functions for PEI) and also with skeleton aliphatic carbons are noticed. But another population (polymer loops and tails) also exists onto silica, characteristic of a physisorbed polymer. The multilayer presence was showed in two ways:

- First, when the amount of polymer adsorbed decreases, the chemical interactions are more obvious in the spectrum. This is due to a decrease of physically polymer multilayers.

- Second, when P4VP-coated beads are immersed in water, interactions between physically adsorbed P4VP and water become predominant, compared to silica interactions due to chemically adsorbed polymer.

REFERENCES

1. R. Rosset, *Bull. Soc. Chim. Fr.,* **6,** 1128 (1985).
2. A. J. Alpert and F. E. Regnier, *J. Chromatogr.,* **185,** 375 (1978).
3. L. Letot, J. Lesec, and C. Quivoron, *J. Liq. Chromatogr.,* **4,** 1311 (1981).
4. J. M. H. M. Scheutjens and G. J. Fleer, *J. Phys. Chem.,* **83,** 178 (1979).
5. E. Gailliez-Dégremont, M. Bacquet, and M. Morcellet, *React. Polym.,* to appear.
6. E. Gailliez-Dégremont, M. Bacquet, J. Y. Dauphin, and M. Morcellet, *J. Colloid Interf. Sci.,* to appear.
7. J. B. Berkowitz, M. Yamin, and R. M. Fuoss, *J. Polym. Sci.,* **28,** 69 (1958).
8. C. Amiel and B. Sébille, *J. Colloid Interf. Sci.,* **149,** 481 (1992).
9. M. Handke and W. Mozgawa, *Vib. Spectrosc.,* **5,** 75 (1983).
10. A. Bertoluzza, C. Fagnaro, M. A. Morelli, V. Gottardi, and M. Guglielmi, *J. Non-Cryst. Solids,* **82,** 127 (1986).
11. C. A. M. Mulder and A. A. J. M. Damen, *J. Non-Cryst. Solids,* **93,** 387 (1987).
12. F. L. Galeener, J. C. Mikkelsen, Jr., and N. M. Johnson, in *Proceedings of the International Topical Conference,* Yorktown Heights, NY, S. T. Partelides, Ed., Pergamon, 1978, p. 284.
13. B. Humbert, A. Burneau, J. P. Gallas, and J. C. Lavalley, *J. Non-Cryst. Solids,* **143,** 75 (1992).
14. C. C. Perry, X. Li, and D. N. Waters, *Spectrochim. Acta,* **47A,** 1497 (1991).
15. A. Neppel and I. S. Butler, *Spectrochim. Acta,* **40A,** 1095 (1984).
16. S. F. Simpson and J. M. Harris, *J. Phys. Chem.,* **94,** 4649 (1990).
17. L. Nikiel and T. W. Zerda, *J. Phys. Chem.,* **95,** 4063 (1991).
18. P. J. Hendra, I. D. M. Turner, E. J. Loaden, and M. Stacey, *J. Phys. Chem.,* **78,** 300 (1974).
19. P. J. Hendra, C. Passingham, G. M. Warres, R. Burch, and D. J. Rawlence, *Chem. Phys. Lett.,* **164,** 178 (1989).
20. N. B. Colthup, L. H. Daly, and S. E. Wibberley, *Introduction to Infrared and Raman Spectroscopy,* Academic Press, New York, 1975.
21. F. C. Dollish, W. G. Fateley, and F. F. Bertley, *Characteristic Raman Frequencies of Organic Compounds,* Wiley, New York, 1974.