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Surface-Enhanced Raman Scattering

by

F. J. Boerio

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Surface-enhanced Raman scattering (SERS) is a process in which the Raman scattering cross section of molecules adsorbed onto the surfaces of metals such as silver, copper, and gold is increased by as much as six orders of magnitude. However, the enhancement is short-range and is restricted to the first few layers of molecules adjacent to the surface. As a result, SERS can be used to characterize adsorption of organic compounds onto metals and can be used for non-destructive characterization of interfaces between polymer films and metal substrates as long as the polymer films are not so thick that normal Raman scattering from the bulk of the film is more intense than SERS from the interface. SERS spectra were obtained from bilayers prepared by spin-coating thin films of polymers such as polystyrene onto silver island films and then overcoating them with much thicker films of a second polymer such as polystyrene sulfonate. The spectra were characteristic of the films adjacent to the silver and not the overlayers as long as the thickness of the films adjacent to the substrate was more than about 100 A in thickness. SERS spectra obtained from thick films of an acrylic adhesive spin-coated onto silver were identical to normal Raman spectra of salts

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19. of saccharin, a component of the cure system, and to SERS spectra of saccharin, indicating that saccharin segregated to the adhesive/substrate interface and adsorbed onto the substrate by dissociation.

Surface-Enhanced Raman Scattering

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F. J. Boerio
Department of Materials Science
and Engineering
University of Cincinnati
Cincinnati, Ohio 45221

SUMMARY

Surface-enhanced Raman scattering (SERS) is a process in which the Raman scattering cross section of molecules adsorbed onto the surfaces of metals such as silver, copper, and gold is increased by as much as six orders of magnitude. However, the enhancement is short-range and is restricted to the first few layers of molecules adjacent to the surface. As a result, SERS can be used to characterize adsorption of organic compounds onto metals and can be used for non-destructive characterization of interfaces between polymer films and metal substrates as long as the polymer films are not so thick that normal Raman scattering from the bulk of the film is more intense than SERS from the interface. SERS spectra were obtained from bilayers prepared by spin-coating thin films of polymers such as polystyrene onto silver island films and then overcoating them with much thicker films of a second polymer such as polystyrene sulfonate. The spectra were characteristic of the films adjacent to the silver and not the overlayers as long as the thickness of the films adjacent to the substrate was more than about 100 A in thickness. SERS spectra obtained from thick films of an acrylic adhesive spin-coated onto silver were identical to normal Raman spectra of salts of saccharin, a component of the cure system, and to SERS spectra of saccharin, indicating that saccharin segregated to the adhesive/substrate interface and adsorbed onto the substrate by dissociation.

I. Introduction

Surface-enhanced Raman scattering (SERS) is a phenomenon in which the Raman scattering cross section of molecules adsorbed onto the roughened surfaces of certain metals is enhanced by as much as 10^6 compared to the cross section for normal Raman scattering. Although many theories of SERS have been reported, it now appears that two mechanisms are responsible for most of the enhancement (1). One mechanism is associated with the large electric fields that can exist at the surfaces of metal particles with small radii of curvature and is only obtained for metals for which the complex part of the dielectric constant is small (1). The other mechanism is related to distortions of the polarizability of the adsorbed molecules by formation of charge transfer complexes with the metal surface [1]. Charge transfer complexes are associated with sites of atomic scale roughness on the surface [2]. As a result, enhancement due to the charge-transfer mechanism is restricted to the molecules immediately adjacent to the substrate but enhancement due to electromagnetic mechanisms may extend a few molecular layers away from the metal surface. The important features of SERS are that the enhancement is very large and short range.

SERS was first reported for pyridine adsorbed onto silver electrodes [3]. Since then, SERS has been observed from a large number of other small molecules including benzoic acid [4, 5], terephthalic acid [6], p-nitrobenzoic acid [7-9], and p-aminobenzoic acid [10-12]. SERS has been reported from metals such as copper [13, 14] and gold [13] in addition to silver and

in a number of configurations such as island films [15] and sols [16] in addition to electrochemical cells. An excellent summary of the work done in this field prior to 1982 has been presented [17].

Considerably less attention has been paid to SERS of polymers, at least in part because of the rapid oxidative degradation that is frequently observed for thin polymer films on metals during intense laser irradiation. Recently, however, we have shown that the degradation of polymers during SERS experiments can be controlled by increasing the thickness of the polymer films [18] or by overcoating the films with thicker films of a second polymer which restrict the supply of oxygen at the metal surface [19].

During the course of that work, it was determined that the normal Raman scattering by the bulk of a polymer film a few hundred angstroms in thickness is considerably less intense than the SERS from a film only a few tens of angstroms in thickness deposited on a SERS-active substrate [19]. As a result, SERS has emerged as a powerful new technique for non-destructive determination of the molecular structure of interfaces between polymers and SERS-active metal substrates. The primary purpose of this paper is to describe results that we have obtained using SERS to determine the molecular structure of interphases between bimolecular polymer layers deposited on silver substrates and between model adhesive systems and silver.

II. Experimental

Substrates for SERS were prepared by slow thermal evaporation of silver island films onto glass slides. In some cases, the slides were cleaned by immersion in a mixture of chromic and sulfuric acids for an hour, rinsed, and dried in nitrogen. In other cases, slides were cleaned by immersion in NaOH solutions for one hour, removed, rinsed in dilute hydrochloric acid solutions, and blown dry in a stream of nitrogen. Silver was evaporated onto the slides at a rate of about 1 A per second to a final thickness of about 45 A in a vacuum chamber equipped with sorption, sublimation, and ion pumps and a quartz crystal oscillator thickness monitor.

Polymers such as polystyrene, polystyrene sulfonate, poly (4-vinylpyridine), and poly (α-methylstyrene) were obtained from Aldrich Chemical Company. Diglycidyl ether of bisphenol-A (DER-332) was obtained from Dow Chemical Company. Low molecular weight compounds such as benzoic acid, sodium benzoate, and the sodium salt of o-benzoic sulfimide (saccharin) were also obtained from Aldrich. A model acrylic adhesive system consisting of the monomer triethyleneglycol dimethacrylate (TRIEGMA) and a curing system containing saccharin (BS), acetylphenylhydrazine (APH), and cumene hydroperoxide (CHP) was obtained from Loctite Corporation. All materials were used as-received.

Thin films of the adhesive, polymers, or low molecular weight compounds were deposited on silver island films by spin coating from dilute solutions. In a few cases, films were spun onto silver island films from the undiluted adhesive.

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SERS spectra were obtained using a spect. meter equipped with a Spex 1401 double monochromator, ITT FW-130 photomultiplier tube, Harshaw photon counting electronics, and a Spectra-Physics Model 165 argon-ion laser. The slits of the monochromator were set for a spectral resolution of 10 cm^{-1}. The laser beam was incident on the SERS samples at an angle of 65° relative to the normal to the sample surface and was polarized perpendicular to the plane of incidence. Scattered light was collected by an f/0.95 lens and focussed onto the entrance slit of the monochromator. Spectra were obtained using the 5145 A line of the laser, a scan rate of 50 cm^{-1}/min, and time constant of 10 sec.

Normal Raman spectra were obtained using the same instrument and techniques that have been described previously [20]. The laser beam was focussed onto a small amount of liquid or powdered sample supported in a capillary tube and the scattered light was collected as described above. However, in this case the spectral slit width was about 2 cm^{-1}.

III. Results and Discussion

A. *SERS from polymer bilayers deposited on silver*

As indicated previously, relatively few investigations of SERS by polymers have been reported. The reasons are at least partly related to catalysis effects by the substrates. When thin films of many polymers are deposited onto silver island films and exposed to intense laser irradiation during SERS experiments, an oxidative degradation reaction occurs resulting in the formation

of graphite-like species and the appearance of strong, broad bands near 1600 and 1400 cm^{-1} [18, 19, 21].

For example, when poly (α-methylstyrene) films were spin-coated onto silver islands and then irradiated at different laser powers, the SERS spectra shown in Figure 1 were obtained. When the laser power was low, the Raman lines from poly (α-methylstyrene) near 1040 and 1010 cm^{-1} were weak as were the lines due to graphitic species near 1600 and 1400 cm^{-1}. As the power was increased, the intensity of the lines near 1040 and 1010 cm^{-1} increased but that of the lines near 1600 and 1400 cm^{-1} increased faster.

The oxidation of polymers during SERS experiments is a free radical process and can be inhibited by blending a small amount of an oxidation inhibitor such as 4-methyl-2,6-di-tert-butyl phenol with the polymer before it is spun onto the SERS substrate [18]. However, the oxidation can also be inhibited by simply increasing the thickness of the polymer film [18]. Thus, the SERS spectra shown in Figure 2 were obtained from films of poly (α-methylstyrene) that were spun onto silver island films from solutions having different concentrations. The bands near 1600 and 1400 cm^{-1} were weakest for films spun from the most concentrated solutions, indicating that those films underwent the least oxidation. It was concluded that thicker films inhibited oxidation by excluding oxygen from the surface of the substrate.

It is interesting to note that the intensity of the Raman lines of poly (α-methylstyrene) near 1040 and 1010 cm^{-1} is approximately the same for all the spectra shown in Figure 2 even

though the sample films differed in thickness by approximately an order of magnitude. This demonstrates that the Raman signal observed in these experiments is independent of the thickness of the sample films and is a characteristic of the interface. Thus it may also be concluded that SERS can be used as a non-destructive technique to determine the structure of polymer/metal interfaces.

The strong Raman lines observed near 940 and 640 cm^{-1} in the spectra shown in Figure 2 are due to sulfite species and are artifacts of the sample preparation process. As discussed above, we sometimes prepare samples by evaporating silver island films onto glass slides that have been cleaned in a mixture of chromic and sulfuric acids. However, it is difficult to remove all of the sulfate ions from the glass surface by rinsing. Some sulfate ions are adsorbed onto the silver and reduced to sulfite during laser irradiation.

The results shown in Figure 2 indicate that the Raman signal in SERS experiments on polymer films originates mostly from the interface and is independent of the thickness of the polymer films. We therefore considered that the SERS signal from bilayers prepared by spinning a thin film of one polymer onto a silver island film and then overcoating it with a second film of a different polymer would consist mostly of scattering from the first film.

The SERS spectra shown in Figure 3 were obtained from bilayers prepared by spinning thin films of polystyrene onto silver island films from acetone solution and then overcoating

them with much thicker films of polystyrene sulfonate (PSS) spun from aqueous solutions [19]. Bands near 1040 and 1010 cm^{-1} are characteristic of polystyrene while a band near 1140 cm^{-1} is characteristic of polystyrene sulfonate. Considering the spectra shown in Figure 3, it is evident that the bands characteristic of polystyrene (1040 and 1010 cm^{-1}) and polystyrene sulfonate [1140 cm^{-1}] were observed when the polystyrene films were spun from the most dilute solutions. However, only the bands near 1040 and 1010 cm^{-1} that were characteristic of polystyrene were observed when polystyrene films were spun from the most concentrated solutions.

Similar results were obtained for other bilayers. The spectra obtained from bilayers prepared by spinning thin films of poly (4-vinylpyridine) (PVP) onto silver island films from dilute solutions in ethanol and then overcoating them with thicker films of polystyrene sulfonate spun from aqueous solutions are shown in Figure 4 [19]. Bands characteristic of poly (4-vinylpyridine) were observed in all the spectra. However, the band characteristic of polystyrene sulfonate near 1140 cm^{-1} was only observed when the PVP films were spun from the solutions having the lowest concentrations.

Another example is shown in Figure 5 for thin films of the diglycidyl ether of bisphenol-A (DGEBA) spun onto silver islands from solutions in acetone and then overcoated with films of PSS spun from aqueous solutions [19]. Raman spectra of DGEBA are characterized by bands near 1120 and 840 cm^{-1} while, as noted above, spectra of PSS are characterized by bands near 1140 and

820 cm^{-1}. Reference to Figure 5 indicates that the Raman lines of the PSS overlayer were observed only when the DGEBA films were spun from the most dilute solutions. When DGEBA films were spun from more concentrated solutions, only the Raman lines near 1120 and 840 cm^{-1} that were characteristic of DGEBA were observed.

The results presented in Figures 3-5 confirm another important characteristic of SERS from polymers. The observed Raman signal is characteristic of the molecules adjacent to the surface and not of the bulk films. This indicates that SERS can be used for the non-destructive characterization of polymer/metal interfaces without interference from normal Raman scattering by the bulk of the polymer.

B. *SERS from a model acrylic adhesive system deposited on silver*

In order to test the application of SERS to the analysis of polymer/metal interfaces, we next considered the model anaerobic acrylic adhesive consisting of the monomer TRIEGMA and a redox cure system composed of APH, saccharin or BS, and CHP [22]. This adhesive is known to cure rapidly in the absence of oxygen and in the presence of certain metals such as copper and iron. However, cure in the presence of other metals such as aluminum and zinc is much slower. We were interested in determining how the cure rate was related to the interfacial chemistry.

Films were spun onto silver island films from the neat adhesive and from 1% and 5% solutions of the adhesive in acetone. The SERS spectra obtained from the films are shown in Figure 6. There are several interesting aspects to these spectra. First, the spectra all have approximately the same intensity even though

the films from which they were obtained had much different thicknesses. This indicates once again that the SERS signal observed from relatively thick polymer films is characteristic of the interface and not of the bulk films. Moreover, the SERS spectra observed for the acrylic adhesive have little resemblance to normal Raman spectra of the monomer. Instead, they are similar to SERS spectra of saccharin (see Figure 7).

Normal Raman spectra of saccharin are characterized by an intense band near 1720 cm^{-1} that is assigned to the stretching mode of the carbonyl group. However, the band near 1720 cm^{-1} is not observed in normal Raman spectra of salts.

SERS spectra of saccharin and of the adhesive are essentially identical to normal Raman spectra of the saccharin salt. This indicates that saccharin in the adhesive segregates to the interface and adsorbs by dissociation to form a salt.

The SERS spectra shown in Figure 8 were obtained when saccharin was replaced in the adhesive with benzoic acid and the adhesive was spun onto a silver island film from a 1% solution in acetone. These spectra are virtually identical to SERS spectra of benzoic acid, indicating again that acidic compounds from the adhesive preferentially adsorb onto the metal substrate by dissociation to form metal salts.

Results that we have obtained from x-ray photoelectron spectroscopy (XPS) confirm that saccharin segregates to the interface and forms salts during curing [23]. Salt formation is also observed when saccharin is simply spin coated onto polished metal substrates from dilute solutions in acetone [23]. The

metal ions in the salts of copper and iron may accelerate polymerization of the monomer by undergoing oxidation while CHP is reduced to form radical anions which initiate polymerization.

$$M^{+n} \rightarrow M^{+(n+1)} + e^- \tag{1}$$

$$\text{(2)}$$
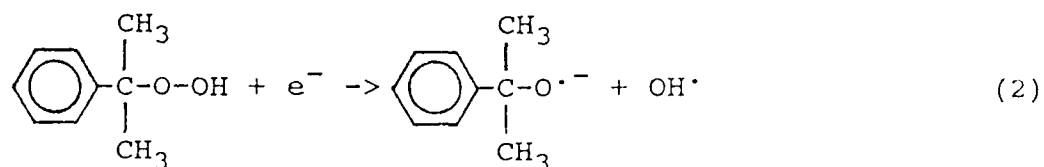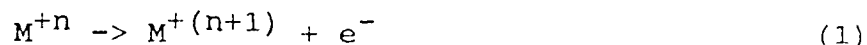
APH may accelerate the cure by breaking down at the metal surface to form radicals which also initiate polymerization. APH may also oxidize while metal ions are reduced to their original

$$M^{+(n+1)} + e^- \rightarrow M^{+n} \tag{3}$$

valence state, thus enabling reaction (2) to be repeated. However, more work will be required in order to elucidate this and other aspects of the polymerization of the acrylic adhesive.

IV. Conclusions

In surface-enhanced Raman scattering, the Raman scattering cross section of molecules adsorbed at the surfaces of metals such as silver, gold, and copper is increased by up to 10^6. However, the enhancement is confined to the first few adsorbed layers. SERS can, therefore, be used for the non-destructive characterization of interfaces between polymer films and metals as long as the thickness of the polymer films is not so great that normal Raman scattering by the bulk films is comparable in intensity to the SERS from the interface. The thickness of polymer film at which that happens depends on the Raman cross section of the polymer and we have not carried out careful

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determinations. However, present results indicate that films as thick as about 1,000 A can be examined.

The use of SERS for determining the structure of polymer/metal interfaces has been demonstrated using bilayers. When thin films of polymers such as poly (α-methylstyrene) were spun onto silver islands and overcoated with thick films of polymers such as polystyrene sulfonate, the observed SERS was characteristic of the first film rather than the overlayer.

SERS spectra obtained from an acrylic anaerobic adhesive system cured against silver were similar to normal Raman spectra of salts of acidic components of the cure system such as o-benzoic sulfimide (saccharin) and benzoic acid. These results indicated that the acids segregated to the interface and adsorbed dissociatively. The metal ions in the salts are thought to have an important role in the redox cure of the adhesive.

V. Acknowledgements

VI. References

1. H. Metiu, in R. K. Chang and T. E. Furtak (eds.), Surface-Enhanced Raman Scattering, Plenum Press, New York, 1982, p. 1.

2. C. Pettenkofer, J. Eickmans, U. Erturk, and A. Otto, Surf. Sci., 151 (1985) 9.

3. D. J. Jeanmaire and R. P. van Duyne J. Electroanal. Chem., 84 (1977) 1.

4. C. Y. Chen, I. Davoli, G. Ritchie, and E. Burstein, Surf. Sci., 101 (1980) 363.

5. W. Chaozi, H. Tianjing, G. Xiaoping, X. Jungqing, X. Houwen, and L. Fan-Chen, J. Mol. Struc., 140 (1987) 227.

6. M. Moskovits and J. S. Suh, J. Phys. Chem., 88 (1984) 1293.

7. R. Dornhaus, R. E. Benner, R. K. Chang, and I. Chabay, Surf. Sci., 101 (1980) 367.

8. C. A. Murray, D. L. Allara, and M. Rhinewine, Phys. Rev. Lett., 46 (1981) 57.

9. P. G. Roth, R. S. Venkatachalam, and F. J. Boerio, J. Chem. Phys., 85 (1986) 1150.

10. J. S. Suh, D. P. DiLella, and M. Moskovits, J. Phys. Chem., 87 (1983) 1540.

11. J. C. Tsang, P. Avouris, and J. R. Kirtley, J. Chem. Phys., 79 (1983) 493.

12. R. S. Venkatachalam, F. J. Boerio, and P. G. Roth, J. Raman Spectrosc., 19 (1987) 281.

13. L. D. Ladouceur, D. E. Tevault, and R. R. Smardzewski, J. Chem. Phys. 78 (1983) 980.

14. S. K. Miller, A. Baiker, M. Meier, and A. Wokaun, J. Chem. Soc., Farad. Trans. I, 80 (1984) 1305.

15. D. A. Weitz, S. Garoff, J. I. Gersten, and A. Nitzan, J. Chem. Phys., 78 (1983) 5324.

16. J. A. Creighton, C. G. Blatchford, and M. G. Albrecht, J. Chem. Soc., Farad. Trans. II, 75 (1979) 790.

17. R. K. Chang and T. E. Furtak, Surface-Enhanced Raman Scattering, Plenum Press, New York, 1982.

18. F. J. Boerio, W. H. Tsai, W. H., and G. Montaudo, J. Polymer

Sci.: Part B: Polymer Phys., in press, 1989.

19. R. S. Venkatachalam, F. J. Boerio, P. G. Roth, and W. H. Tsai, J. Polymer Sci.: Part B: Polymer Phys., 26 (1988) 2447.

20. F. J. Boerio and J. L. Koenig, J. Polymer Sci.: Polymer Symposia, 43 (1973) 205.

21. R. S. Venkatachalam, F. J. Boerio, M. R. Carnevale, and P. G. Roth, Appl. Spectrosc., 42 (1988) 1207.

22. F. J. Boerio and P. P. Hong, Langmuir, submitted for publication, 1989.
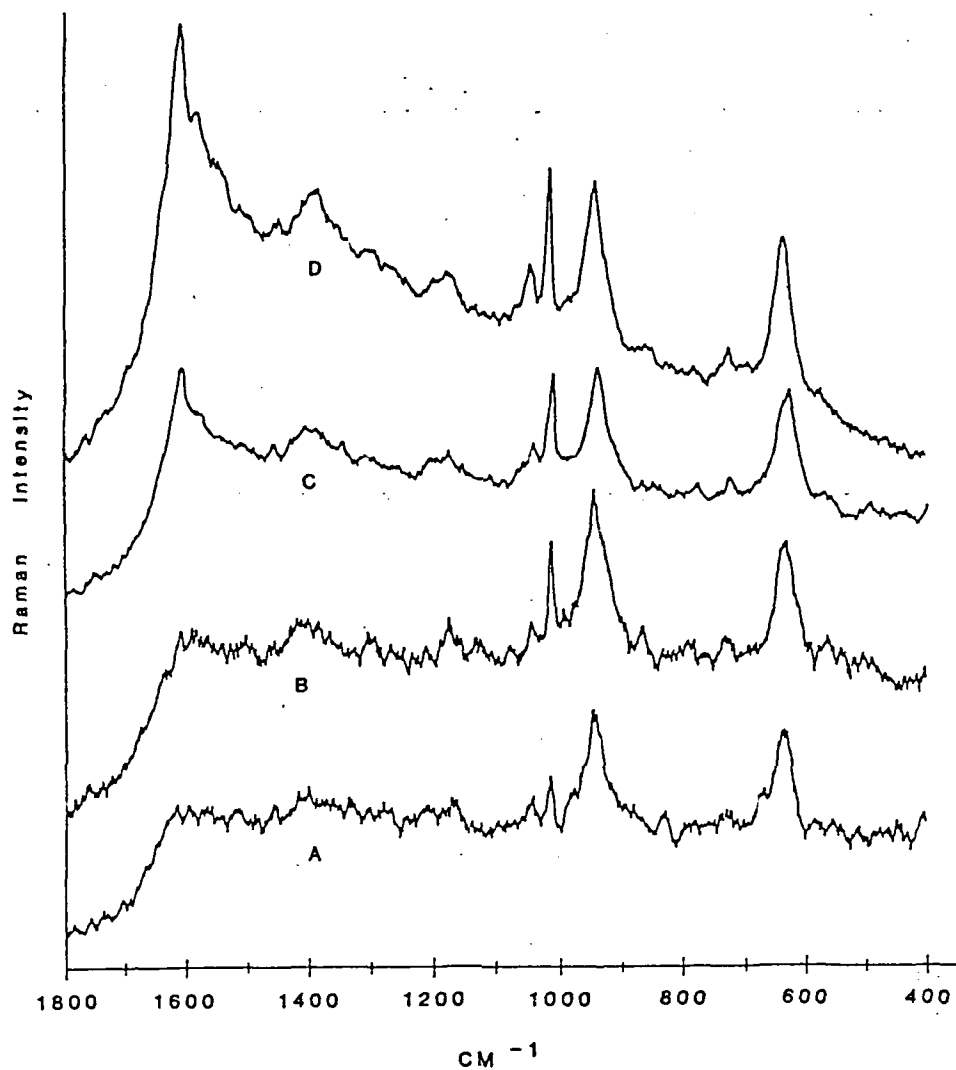
23. S. J. Hudak, and F. J. Boerio, to be published, 1989.

Figure 1. SERS spectra obtained from poly (α-methylstyrene)
films spin-coated onto silver island films from 1%
MEK solutions. The laser power was (A)-10, (B)- 25,
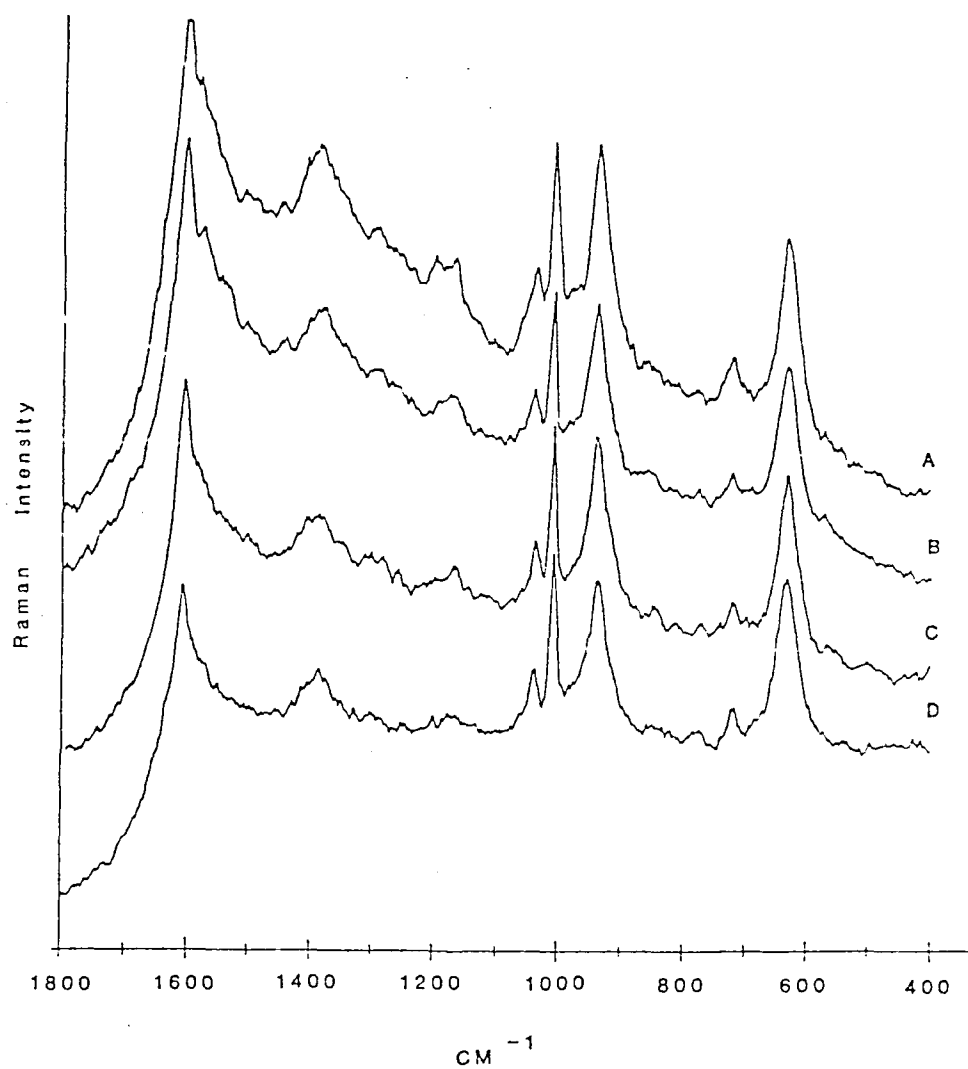(C)-50, and (D)-100 mW. Reprinted with permission
from reference 18.

Raman Intensity

1800 1600 1400 1200 1000 800 600 400

CM^{-1}

Figure 2. SERS spectra obtained from poly (α-methylstyrene) films spun onto silver island films from MEK solutions having concentrations of (A)-0.5, (B)-1.0, (C)-2.0, and (D)-5%. The laser power was 100 mW in all cases. Reprinted with permission from reference 18.
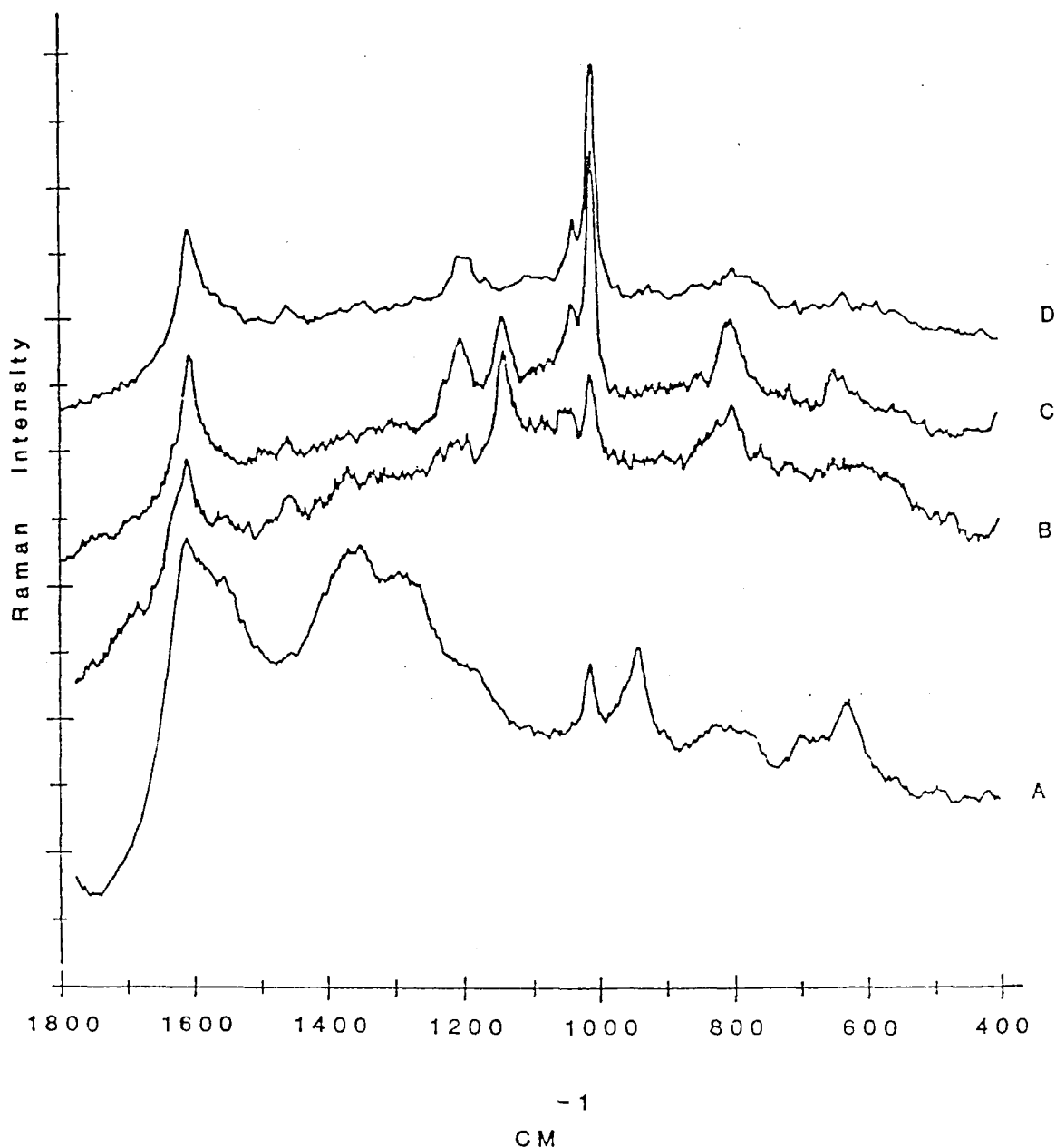
Figure 3.   Surface-enhanced Raman spectra obtained from
            polystyrene films spin-coated onto silver island films
            from (B)-0.025%, (C)-0.05%, and (D)-0.1% solutions in
            MEK and overcoated with polystyrene sulfonate films
            spun from 2% aqueous solutions.   The sample used to
            obtain spectrum A was similar to that used for B but
            without the overlayer.   Reprinted with permission from
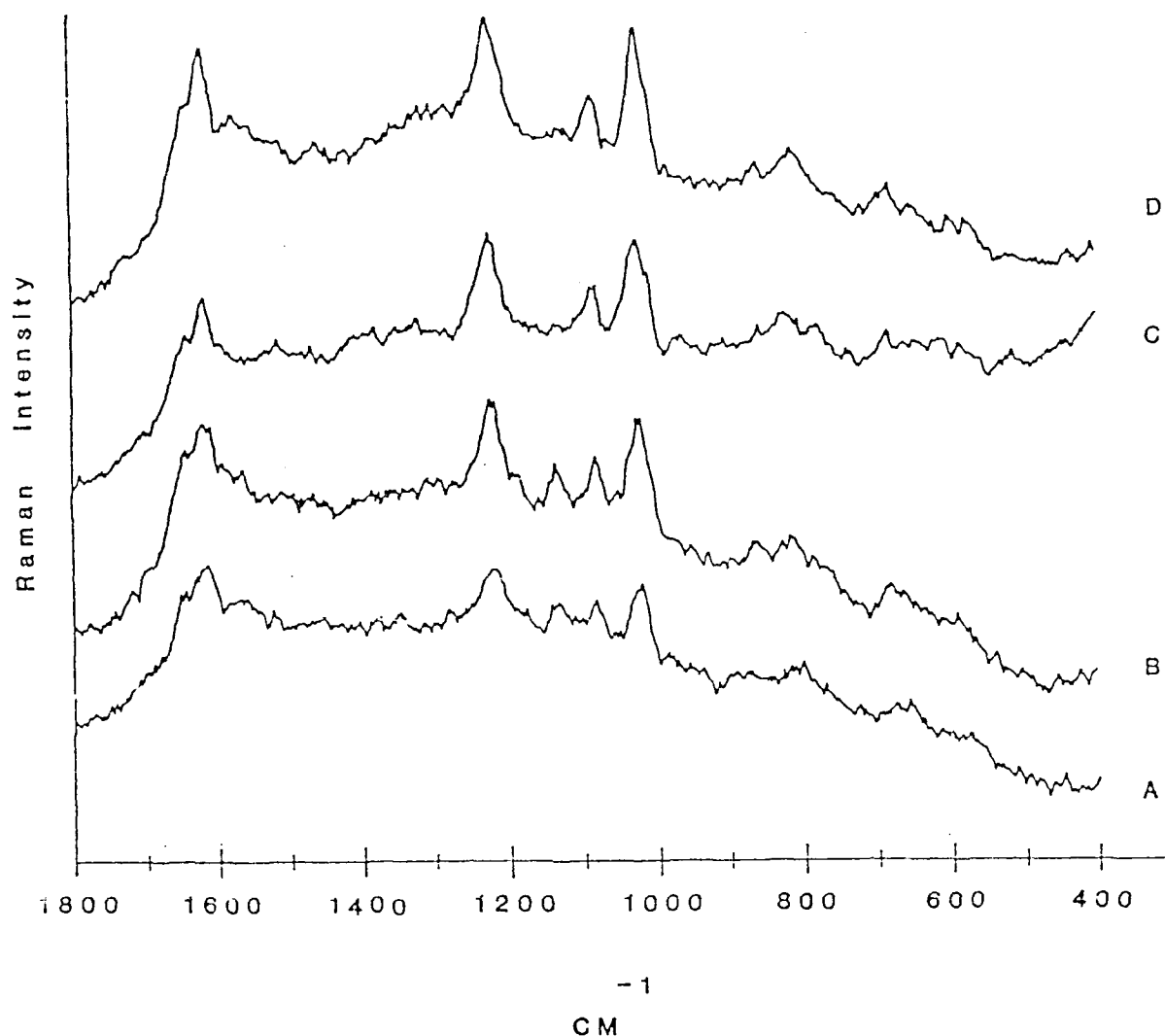   reference 19.

Figure 4. Surface-enhanced Raman spectra obtained from poly (4-vinyl pyridine) films spin-coated onto silver island films from (A)-0.0125%, (B)-0.025%, (C)-0.05%, and (D)-0.1% solutions in MEK and overcoated with polystyrene sulfonate spun from 0.75% aqueous solutions. Reprinted with permission from reference 19.
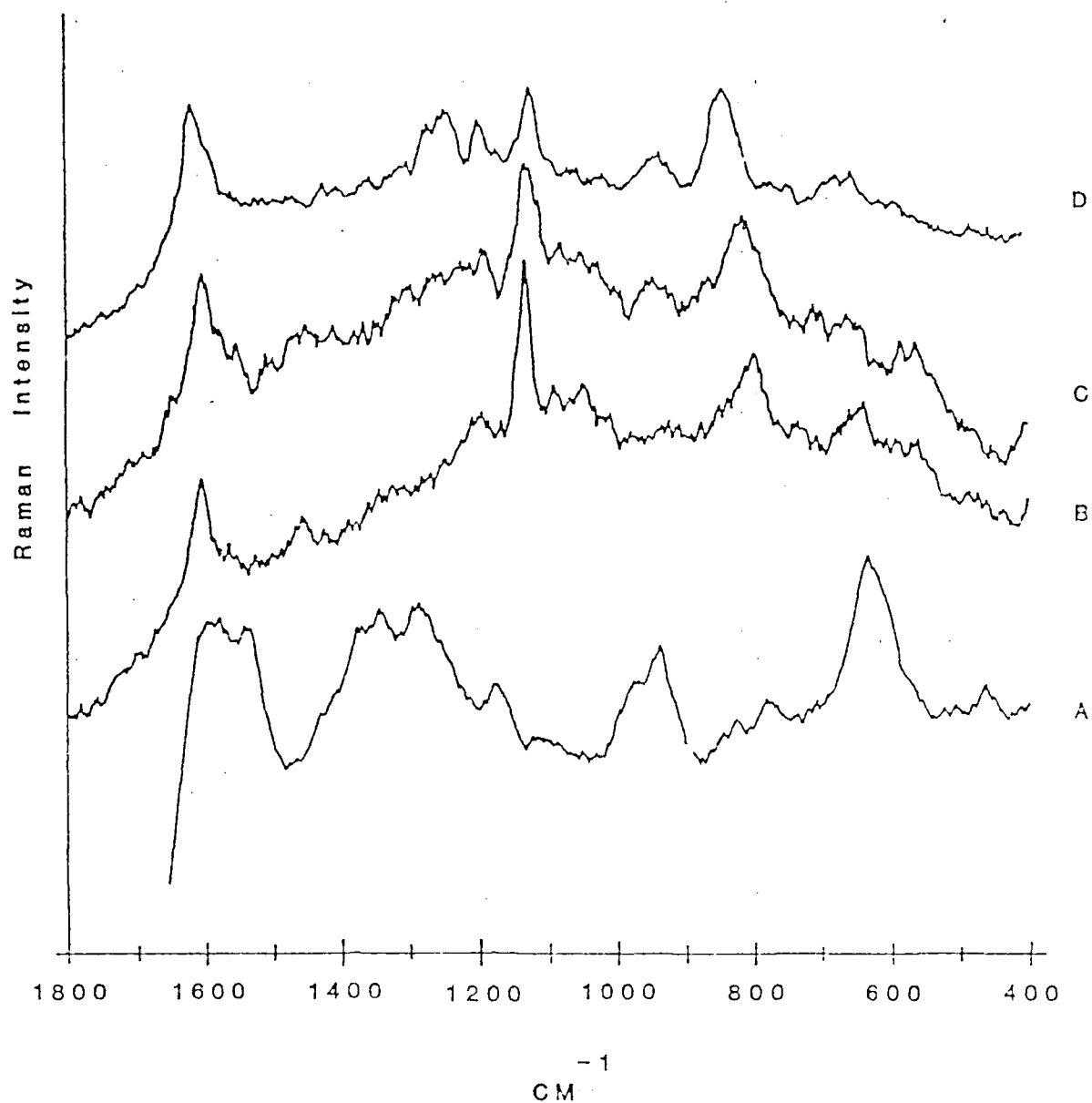
Figure 5. Surface-enhanced Raman spectra obtained from DGEBA
films spin-coated onto silver island films from (B)-
0.01%, (C)-0.05%, and (D)-0.1% solutions in MEK and
overcoated with polystyrene sulfonate films spun from
2% aqueous solutions. The sample used to obtain
spectrum A was similar to that used for B but without
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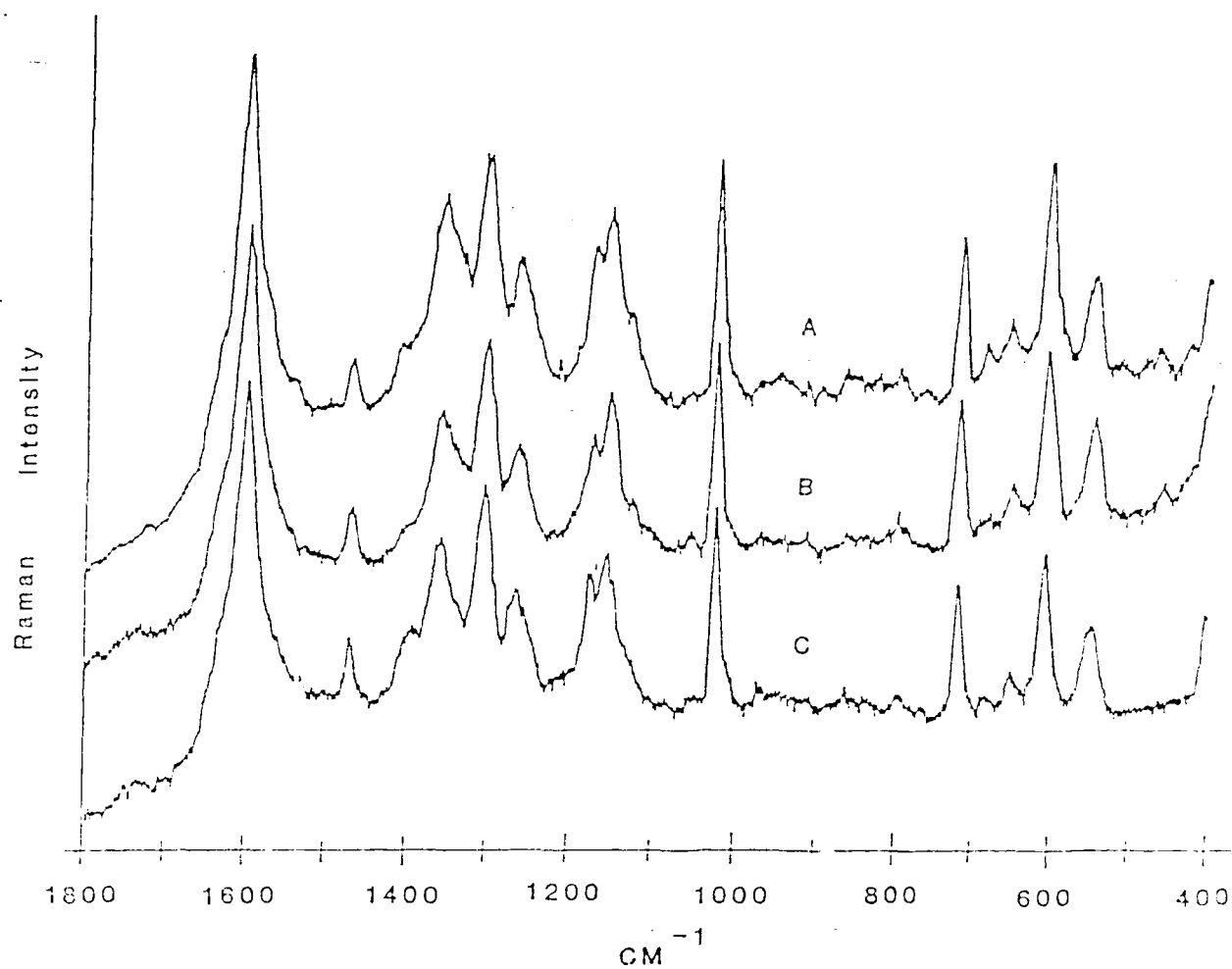reference 19.

Figure 6. SERS spectra obtained when acrylic adhesive was spin-
coated onto silver island films from (A) - 1% and (B)
- 5% solutions in acetone and (C) - from the bulk.
The laser power was 100 mW in all cases. Reprinted
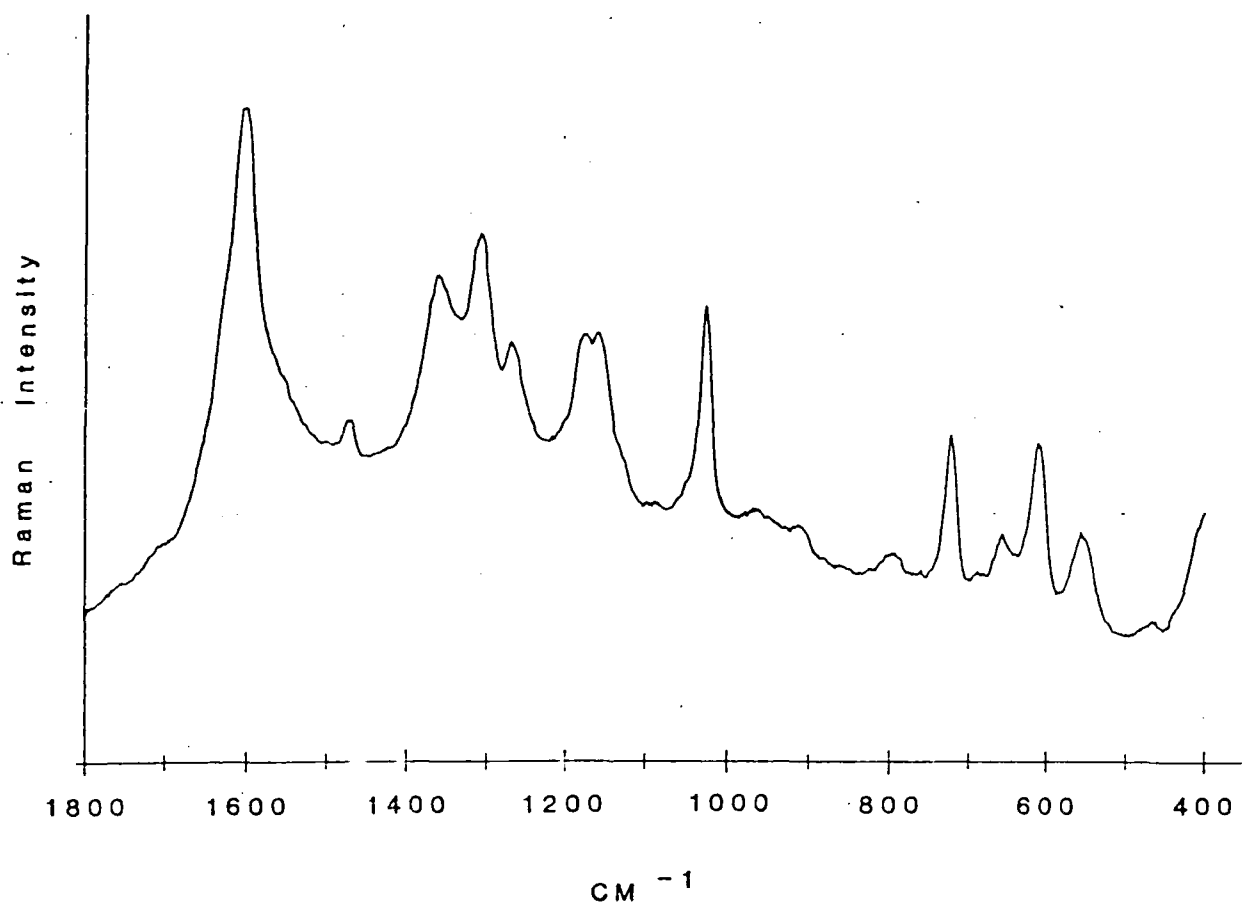with permission from reference from reference 22.

Figure 7. SERS spectra from saccharin spin-coated onto a silver island film from a 0.1% acetone silution. The laser power was 100 mW. Reprinted with permission from reference 22.
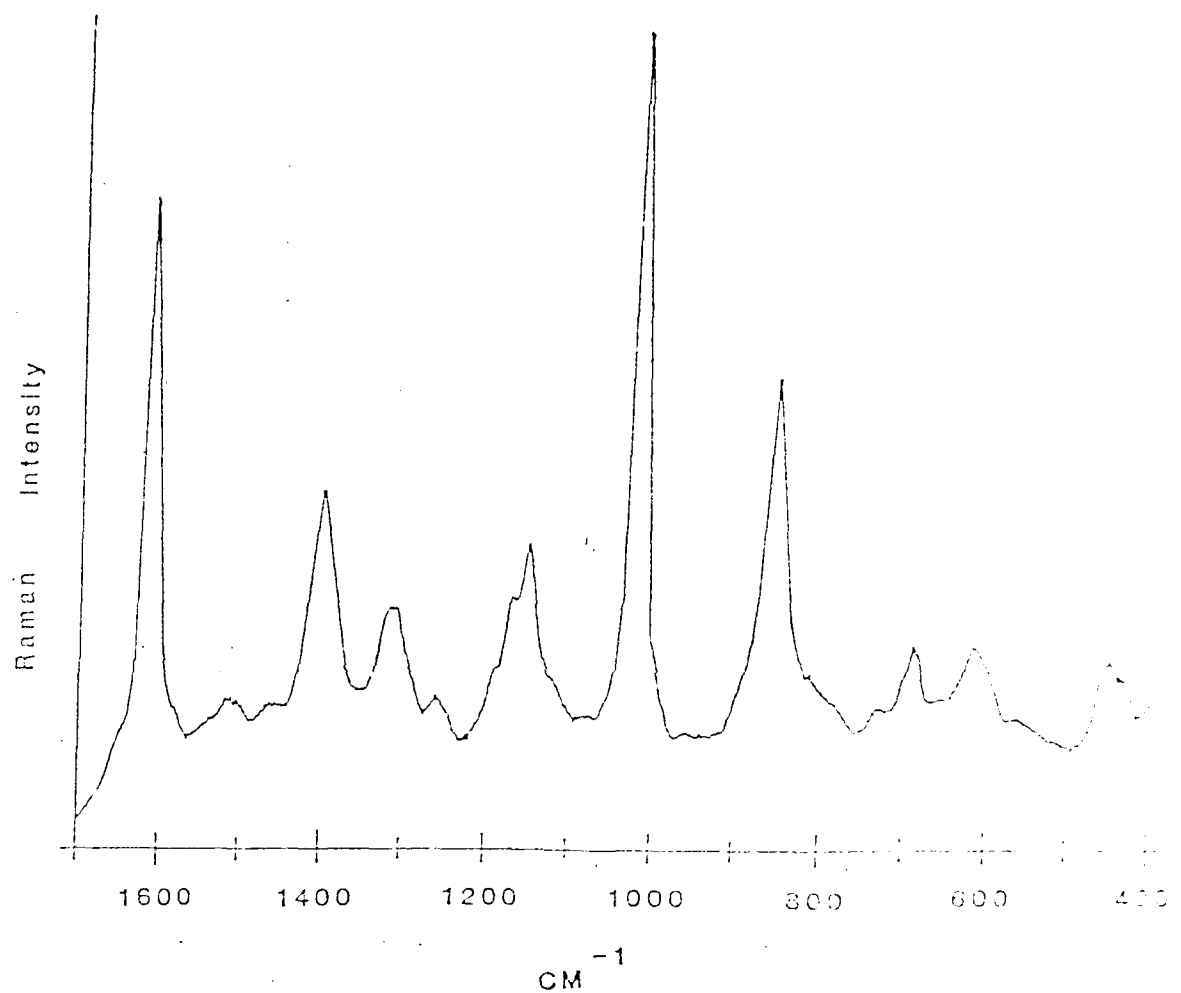
Figure 8.   SERS spectra obtained when the acrylic adhesive with benzoic acid substituted for saccharin was applied to a silver island film and allowed to cure. The laser power was 100 mW. Reprinted with permission from reference 22.

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