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Non-Destructive Characterization of Polymer/Metal Interphases Using Surface-Enhanced Raman Scattering

by

F. J. Boerio, P. P. Hong, W. H. Tsai, and J. T. Young

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Surface-enhanced Raman scattering (SERS) is an analytical technique in which the Raman scattering cross sections of molecules adsorbed onto the roughened surfaces of certain metals are enhanced by as much as six orders of magnitude compared to their value for normal Raman scattering. The mechanisms are associated with the large electric fields that can be induced at the surfaces of metal particles having small radii of curvature and with formation of charge transfer complexes between the adsorbed molecules and the substrate. Enhancement due to the charge transfer mechanism is obtained only for molecules immediately adjacent to the surface but enhancement due to the electromagnetic mechanism may extend several monolayers away from the surface. Since normal Raman scattering by polymers is weak and scattering by molecules adjacent to the substrate is strongly enhanced, SERS can be used for non-destructive characterization of interfaces between polymer films and metals as long as the films are not so thick that scattering by the bulk of the film

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is comparable in intensity to SERS from the interface.

We have used SERS to examine the interface between silver and an acrylic adhesive system consisting of an acrylic monomer and a cure system consisting of cumene hydroperoxide (CHP), acetylphenylhydrazine (APH), and saccharin. SERS spectra obtained from films of the adhesive spin-coated onto silver island films were similar to normal Raman spectra of salts of saccharin, indicating that saccharin had adsorbed on the silver dissociatively. The spectra were independent of the thickness of the adhesive films, indicating that the SERS signal was characteristic of the interface and not of the bulk adhesive.

SERS has also been used to characterize the interface between silver and pyromellitic diimide (PMDI), a model compound for polyimides. SERS spectra of PMDI adsorbed onto silver were considerably different from normal Raman spectra. The strongest band in the normal spectra, a carbonyl stretching mode near 1770 cm^{-1}, was absent from the SERS spectra and a band near 700 cm^{-1} which was very weak in normal Raman spectra was strong in SERS spectra. It was concluded that PMDI was adsorbed with a vertical conformation with one imide group adjacent to the surface.

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ABSTRACT

Surface-enhanced Raman scattering (SERS) is an analytical technique in which the Raman scattering cross sections of molecules adsorbed onto the roughened surfaces of certain metals are enhanced by as much as six orders of magnitude compared to their value for normal Raman scattering. The mechanisms are associated with the large electric fields that can be induced at the surfaces of metal particles having small radii of curvature and with formation of charge transfer complexes between the adsorbed molecules and the substrate. Enhancement due to the charge transfer mechanism is obtained only for molecules immediately adjacent to the surface but enhancement due to the electromagnetic mechanism may extend several monolayers away from the surface. Since normal Raman scattering by polymers is weak and scattering by molecules adjacent to the substrate is strongly enhanced, SERS can be used for non-destructive characterization of interfaces between polymer films and metals as long as the films are not so thick that scattering by the bulk of the film is comparable in intensity to SERS from the interface.

We have used SERS to examine the interface between silver and an acrylic adhesive system consisting of an acrylic monomer and a cure system consisting of cumene hydroperoxide (CHP), acetylphenylhydrazine (APH), and saccharin. SERS spectra obtained from films of the adhesive spin-coated onto silver island films were similar to normal Raman spectra of salts of saccharin, indicating that saccharin had adsorbed on the silver dissociatively. The spectra were independent of the thickness of

the adhesive films, indicating that the SERS signal was characteristic of the interface and not of the bulk adhesive.

SERS has also been used to characterize the interface between silver and pyromellitic diimide (PMDI), a model compound for polyimides. SERS spectra of PMDI adsorbed onto silver were considerably different from normal Raman spectra. The strongest band in the normal spectra, a carbonyl stretching mode near 1770 cm^{-1}, was absent from the SERS spectra and a band near 700 cm^{-1} which was very weak in normal Raman spectra was strong in SERS spectra. It was concluded that PMDI was adsorbed with a vertical conformation with one imide group adjacent to the surface.

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 as much as 10^6 compared to the normal Raman scattering cross section. Two mechanisms seem to be responsible for most of the enhancement. One 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 is related to distortions of the polarizability of the adsorbed molecules by formation of charge-transfer complexes with the metal surface (1). 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 several tens of angstroms from the metal surface.

Since the enhancement in SERS is very large but restricted to the first few molecular layers adjacent to the substrate, we considered that SERS would be an extremely effective technique for non-destructive determination of the molecular structure of interphases between polymer systems and metals. We investigated SERS from thin films of poly (α-methylstyrene) spin coated onto silver island films from dilute solutions and found that the intensity of the spectra remained approximately constant when the thickness of the films was varied by an order of magnitude (2). These results demonstrated that SERS from the polymer films was an interfacial rather than bulk effect (2). The normal Raman scattering by the bulk of the polymer film was so weak it was not observed as long as the film was thinner than approximately a thousand angstroms. What was observed was the strongly enhanced scattering by the molecules adjacent to the silver surface.

We also investigated SERS from polymer bilayers deposited on silver island films (3). Samples were prepared by spin-coating thin films (approximately 100 A) of polymers such as polystyrene, poly (α-methylstyrene), poly (4-vinylpyridine), and diglycidyl ether of bisphenol-A onto silver substrates and then overcoating them with much thicker films of a second polymer such as poly (4-styrene sulfonate). The results confirmed that SERS could be used for non-destructive characterization of interphases. Raman scattering was observed from both polymers as long as the thickness of the film adjacent to the silver was less than about 100 A in thickness. However, Raman scattering was observed from the polymer adjacent to the silver but not from poly (4-styrene sulfonate) when the thickness of the film adjacent to the substrate was more than about 100 A in thickness.

SERS can also be used to determine the orientation of adsorbed molecules. Several authors have investigated the selection rules for Raman scattering by molecules adsorbed onto metal substrates. Moskovits developed a theory that was based on electromagnetic effects (4). According to the theory, modes which are normally allowed for the free molecule may appear in surface spectra with considerably different intensities. The strongest lines in the Raman spectra of molecules adsorbed onto metal substrates should correspond to modes that transform the same as α_{zz} where z is the coordinate perpendicular to the metal surface. The next most intense lines should correspond to modes transforming as α_{xz} and α_{yz}. The weakest lines should correspond to modes tranforming as α_{xy}, α_{xx}, and α_{yy}. Modes transforming as α_{zz} and involving atomic motions mostly perpendicular to the surface were predicted to be especially intense.

Modes which are normally forbidden may appear in the Raman spectra of molecules adsorbed on the surfaces of reflecting substrates for two reasons (5). One is that the high symmetry molecule may become a lower symmetry surface complex. The other is that quadrupole terms may contribute to the molecular polarizability. Thus, by comparing the relative intensities of the bands in the normal Raman spectra with those in the SERS spectra and taking into account the predictions of the theories described above, the orientation of adsorbed molecules can be determined.

Hallmark and Campion investigated normal Raman scattering from benzene-d_6, pyrazine, and s-triazine physically adsorbed onto the (111) and (110) faces of single crystal silver (5). The spectra were interpreted by involving the adsite geometry and image dipole effects in the surface selection rules. Quadrupole interactions were neither necessary nor sufficient to predict the surface spectra.

Strong bands were observed near 945 and 495 cm^{-1} in Raman spectra of benzene-d_6 adsorbed on the (111) face of silver. The band near 495 cm^{-1} was assigned to mode $\nu(11)$ in the Wilson numbering system (6) which belongs to the species A_{2u} and is normally forbidden for free molecules having D_{6h} symmetry. The appearance of this band in the surface spectra was interpreted to mean that benzene was adsorbed with its ring parallel to the surface and that the molecular symmetry was reduced to C_{2v}. Under C_{2v} symmetry, mode $\nu(11)$ belongs to the symmetry species A_1 and is Raman active.

Raman spectra were also obtained of benzene-d_6 adsorbed onto the Ag (111) surface at different coverages. Only the bands near 945 and 495 cm^{-1} were observed for submonolayer coverage. However, additional bands appeared near 860, 665, and 580 cm^{-1} in the spectra of multilayers. The bands near 860 and 580 cm^{-1} were assigned to the E_{2g} modes $\nu(9)$ and $\nu(6)$, respectively, while the band near 665 cm^{-1} was assigned to $\nu(10)$. The appearance of these bands was attributed to molecules in multilayers adsorbing with their rings tilted with respect to the surface. Moreover, the intensity of the band due to $\nu(11)$ was essentially the same for submonolayer and multilayer coverages, indicating that its activity was related to a first layer effect.

Hallmark and Campion also obtained normal Raman spectra from pyrazine and s-triazine adsorbed onto Ag(111) and Ag(110) surfaces (5). At submonolayer coverages, both compounds adsorbed on Ag(111) with a flat configuration and on Ag(110) with a vertical (end-on) conformation.

Moskovits, DiLella, and Maynard investigated SERS from several aromatic molecules adsorbed onto silver surfaces (7). For s-triazine, the intensity of bands assigned to out-of-plane modes decreased relative to that of bands assigned to in-plane modes as the time of laser irradiation increased. α_{zz} was considered to be large for out-of-plane vibrations of molecules having the flat geometry on the surface but small for out-of-plane modes of molecules having the vertical (end-on) geometry. It was concluded that the observed changes were due to laser-induced reorientation in which some molecules changed from the flat to the end-on geometry.

Moskovits, DiLella, and Maynard also obtained SERS spectra of pyrazine for two different coverages and observed differences attributed to molecular orientation. The intensity of the band assigned to $\nu(8a)$ increased relative to that of the band assigned to $\nu(1)$ as the surface coverage was increased. Since mode $\nu(8a)$ mostly involves nuclear motion parallel to the C_2 axis traversing the nitrogen atoms, it was expected to be most enhanced when pyrazine was bound to the surface through one nitrogen atom. It was also observed that the band assigned to $\nu(1)$ shifted from 995 to 1014 cm^{-1} on going from low to high coverage. If pyrazine was adsorbed onto the surface through the π-electrons, the frequency of the ring breathing mode $\nu(1)$ was expected to decrease slightly from its value in the free molecule. Thus, this frequency shift provided further evidence for a flat orientation at low coverage.

Observation of normally forbidden bands in the SERS spectra was interpreted by the field gradient model. This was due to the rapid spatial rate of change in the radiative electric field occurring at sharp features of surface, which resulted in vibrations belonging to the same representation as elements of the dipole-quadrupole tensor becoming Raman active. Moskovits also concluded that the field gradient model seemed to account better for the relative intensities of normally forbidden bands that became active than did the symmetry reduction model based on the formation of a surface complex (7).

We are particularly interested in using SERS for non-destructive characterization of polymer/metal interphases. Anaerobic acrylic adhesives, which are used as thread locking and gasketing compounds, consist of an acrylic monomer and a cure system containing several components. Polymerization of the monomer proceeds by a redox mechanism at ambient temperatures but little is known regarding the mechanisms by which some metals and some components of the cure system accelerate the reaction. Similarly, it is not known how the extent of polymerization varies as a function of distance away from the substrate surface and into the adhesive.

A few investigations of the polymerization of anaerobic acrylic adhesives in solution have been reported. Okamoto (8) investigated the solution polymerization of a model anaerobic adhesive consisting of methyl methacrylate (MMA) monomer with the cure system N,N dimethyl-p-toluidene (DMPT), o-benzoic sulfimide (BS), and cumene hydroperoxide (CHP). He found that the rate of polymerization was given by

$$R_p = [MMA]^{3.3} [BS]^{0.36} [DMPT]^{0.34} [[CHP]^{0} \quad (1)$$

Since only trace amounts of the peroxide CHP were needed to catalyze the reaction, Okamoto speculated that the oxidizing agent in this system was most likely a trace of molecular oxygen and/or hydrogen peroxide. The reducing agent appeared to be a charge transfer complex between BS and DMPT.

Kothandaraman and Arumugasamy (9) reported that a charge-transfer complex formed between N,N-dimethylaniline and p-toluene sulphonyl chloride was a redox initiator for polymerization of methyl methacrylate in acetonitrile at 50^{o}C. It was suggested that polymerization was initiated by N-methylanilinomethyl radicals formed by decomposition of the complex. Neither N,N-dimethylaniline nor p-toluene sulphonyl chloride acted as an initiator when used separately.

Parravano (10) investigated the effect of palladium black on polymerization of several monomers by hydrazine sulfate. Rapid polymerization was observed for methyl methacrylate but not for acrylonitrile or methacrylonitrile. It was suggested that polymerization of methyl methacrylate monomer was induced by the catalytic decomposition of hydrazine sulfate at the surface of palladium black. Acrylonitrile and methacrylonitrile acted as poisons to the catalytic decomposition of hydrazine and were not polymerized under similar conditions. Even though polymerization was initiated by decomposition of hydrazine at the surface of palladium black, the reaction would continue if the palladium was isolated from the liquid, indicating that reactions could be initiated at catalyst surfaces and projected into the surrounding medium for propagation.

Little information is available regarding the molecular structure of interphases formed between anaerobic acrylic adhesives and metal substrates. However, Clark (11) used reflection-absorption infrared spectroscopy (RAIR) and x-ray photoelectron spectroscopy (XPS) to characterize the failure surfaces of lap joints prepared using acrylic adhesives and steel and galvanized steel adherends and showed that acidic components of the adhesives segregate to the interface and form salts.

Numerous investigations of the interphase formed by the evaporation of metals onto polyimides prepared from pyromellitic dianhydride (PMDA) and oxydianiline (ODA) have been reported. Rossi (12) carried out molecular orbital calculations on complexes of chromium with the model compound N,N′ - diphenyl-pyromellitic diimide. The results indicated the possible formation of a complex in which Cr atoms were located above the central benzene rings of the PMDA structure. Hahn (13) used XPS to investigate the interaction of chromium, copper, and nickel with PMDA/ODA polyimides and found that nickel and copper diffused into the polyimide but chromium did not. Some evidence was obtained for the formation of complexes between chromium and the polyimide. Recently, van Ooij (14) has used SIMS to determine the interaction of metals with PMDA/ODA polyimides and suggested that chromium attacked the imide groups. Relatively little fundamental information is available regarding interphases formed when polyimides are cured against metals.

The primary purpose of this paper is to describe the use of SERS to determine the molecular structure of polymer/metal interphases. When a model anaerobic acrylic adhesive was cured against a silver substrate, o-benzoic sulfimide (saccharin), a component of the adhesive system, was preferentially adsorbed to form a salt. Formation of these salts is considered to be an essential step in the curing reaction. When pyromellitic diimide (PMDI), a model compound for polyimides, was adsorbed onto silver, large differences between the SERS and normal Raman spectra were observed. These differences were related to the orientation of the adsorbed molecules and to the adsorption mechanism. It was concluded that PMDI molecules were adsorbed with their planes perpendicular to the surface and with one imide group in contact with the surface.

II. Experimental

The acrylic adhesive was a model consisting of the monomer triethyleneglycol dimethacrylate (TRIEGMA), o-benzoic sulfimide (saccharin or BS), acetylphenylhydrazine (APH), and cumene hydroperoxide (CHP) mixed in the ratio 100:0.83:0.70:2.78 parts by weight (15). APH, BS, CHP, and TRIEGMA were supplied by Loctite Corporation and used as-received. TRIEGMA was purified by washing with aqueous NaOH and dried in a rotary evaporator at room temperature in vacuo before shipment. Saccharin and acetylphenylhydrazine were recrystallized from ethanol. Pyromellitic diimide and the sodium salt of saccharin were obtained from Aldrich and used as-received.

Substrates for SERS were prepared by slow thermal evaporation of silver island films onto glass slides. The slides were cleaned by immersion in 0.1N NaOH solutions for one hour, rinsed in 0.1N hydrochloric acid solutions for one hour, rinsed in distilled water in an ultrasonic cleaner, and blown dry in a stream of nitrogen. The slides were immediately placed in a vacuum chamber equipped with sorption, sublimation, and ion pumps and a quartz crystal oscillator thickness monitor and pumping was initiated. When the pressure reached 10^{-6} Torr, silver was evaporated onto the slides at a rate of about 1 A per second to a final thickness of about 45 A.

Thin films of the adhesive and saccharin were deposited on silver island films by spin-coating from dilute solutions in acetone. In a few cases, films were deposited by spinning the undiluted adhesive onto silver island films. Films of PMDI were deposited onto silver island films by spin-coating from dilute solutions in dimethylformamide. Samples were prepared for normal Raman spectroscopy by placing a small amount of sample into a capillary tube.

The thickness of the adhesive films spin-coated onto silver island films was estimated by spinning films from the same solutions onto silver films that were several thousand angstroms in thickness and examining the adhesive films with an ellipsometer.

All of the SERS and normal Raman spectra were obtained using a spectrometer 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. In SERS experiments, the slits of the monochromator were set for a spectral resolution of 10 cm^{-1}. The laser beam was incident on the samples at an angle of 65^{o} relative to the normal to the sample surface and was polarized parallel to the sample surface. Scattered light was collected by an f/0.95 lens and focussed onto the entrance slit of the monochromator. SERS 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. Similar techniques were used for obtaining normal Raman spectra but the slit width was 5 cm^{-1} and the time constant was 2 sec. Ellipsometry was carried out using a Rudolph Research Model 436 Ellipsometer.

III. Results and Discussion

A. *SERS spectra of acrylic adhesive*

SERS spectra shown in Figures 1A and 1B were obtained from films of the acrylic adhesive spin-coated onto silver island films from acetone solutions having concentrations of 1% and 5%, respectively (15). The spectrum shown in Figure 1C was obtained from a film spin-coated from the undiluted adhesive. The spectra were dominated by strong bands near 1600, 1360, 1306, 1175, 1155, 1025, 720, and 609 cm^{-1}. Weaker bands were also observed near 1470, 1266, 658, and 552 cm^{-1}.

It was expected that films spun from the most concentrated solutions would be the thickest and exhibit the most intense Raman scattering. However, reference to Figure 1 shows that the SERS intensities of films spun from 1% and 5% solutions of the adhesive and from the undiluted adhesive were virtually identical even though the thicknesses of the films ranged from approximately 100 A for the film spun from the 1% solution to 500 A for that spun from the adhesive itself (15).

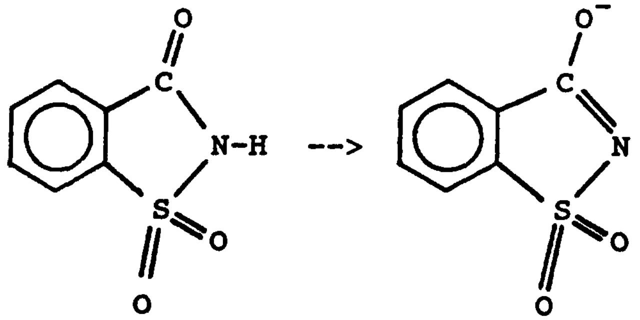
SERS spectra of the adhesive deposited on silver island films were completely different from normal Raman spectra of the monomer (15). Raman spectra of TRIEGMA were characterized by strong bands near 1730 and 1650 cm^{-1} that were assigned to ν(C=O) and ν(C=C), the stretching modes of the CO and CC double bonds, respectively. The band near 1650 cm^{-1} was not expected to appear in SERS spectra of the adhesive due to polymerization of the monomer. The band due to the carbonyl group was expected but was not observed.

SERS spectra of the adhesive were, however, similar to SERS spectra of saccharin (see Figure 2A) and to normal Raman spectra of the sodium salt of saccharin (see Figure 2B). As a result, most of the bands observed in the SERS spectra of the adhesive were assigned to vibrational modes of the sulphonyl group and the substituted benzene ring (15). Three bands characteristic of the sulphonyl group were expected, corresponding to $\nu_s(SO_2)$, $\nu_a(SO_2)$, and $\delta(SO_2)$, the symmetric and asymmetric stretching and deformation modes, respectively. We have assigned the strong bands near 1360 and 1175 cm^{-1} to $\nu_a(SO_2)$ and $\nu_s(SO_2)$, the asymmetric and symmetric stretching modes of the sulphonyl group, respectively. The band near 552 cm^{-1} was assigned to $\delta(SO_2)$, the deformation mode.

Most of the remaining bands observed in the SERS spectra of the adhesive were attributed to vibrations of the benzene ring using the Wilson numbering system (15). Thus, the band near 1600 cm^{-1} was assigned to ν(8a), a tangential ring stretching mode. Bands near 1155 and 1025 cm^{-1} were assigned to the CH in-plane bending modes ν(15) and ν(18b), respectively. ν(1), a radial ring stretching mode, was assigned to the strong band near 720 cm^{-1}. The weak band near 1470 cm^{-1} was attributed to ν(19b), a tangential ring stretching mode, and the band near 609 cm^{-1} was attributed to $\nu(6a)$, a radial ring stretching and bending mode. The strong band near 1308 cm^{-1} and the moderately strong band near 1270 cm^{-1} were attributed to $\nu(14)$, a tangential ring stretching mode, and $\nu(3)$, a CH in-plane bend, respectively.

A strong band characteristic of the C=O stretching mode was observed near 1707 cm^{-1} in normal Raman spectra of saccharin (see Figure 2C). That band was not observed in SERS spectra of the adhesive or saccharin or in normal Raman spectra of the sodium salt of saccharin. However, weak bands were observed near 1658 and 1644 cm^{-1} in spectra of the salt and assigned to a C=N stretching mode.

The SERS spectra of the adhesive were similar to SERS spectra of saccharin and were independent of the film thickness deposited on the silver island films. Thus, it was concluded that the SERS spectra of the adhesive were characteristic of the interface rather than the bulk adhesive and that saccharin, a relatively minor component of the adhesive, segregated to the interface and adsorbed onto the silver surface by dissociation to form a salt as shown below (15):



(2)

It is interesting to note that the intensities of several bands were much greater in the SERS spectra than in the normal Raman spectra. The band near 1600 cm^{-1} assigned to ν(8a) was weak in normal Raman spectra of the salt but was the strongest band in the SERS spectrum. Similarly, the band near 609 cm^{-1}, which was attributed to ν(6a), was weak in normal Raman spectra of the salt but strong in SERS spectra.

As noted above, there are several reasons for bands to have different intensities in SERS and normal Raman spectra. Bands which are "normally allowed" for the free molecule may have considerably different intensities in SERS. According to the theory developed by Moskovits for Raman scattering by molecules near metal surfaces, the strongest bands are related to modes transforming as α_{zz}, where z is perpendicular to the surface, and having motions mostly perpendicular to the metal surface (4). The next most intense bands are those transforming as α_{xz} and α_{yz} while the weakest bands are those transforming as α_{xx}, a_{yy}, and a_{xy}. Bands which are "normally forbidden" under the symmetry of the free molecule may appear in SERS spectra because of a decrease in symmetry brought about by the formation of surface complexes or because of the contribution of higher order terms to the polarizability.

o-Disubstituted benzene rings as in saccharin have at most $C_{2v}{}^*$ symmetry and all of the vibrational modes of the rings are allowed in normal Raman spectra of the free molecule. No normally forbidden modes were expected in the SERS spectra and none were observed. Under $C_{2v}{}^*$ symmetry, modes 1, 2, 6a, 7a, 8a, 9a, 15, 18b, 19b, and 20b transform as α_{zz} (16) and should correspond to the strongest bands in the SERS spectra. However, modes 2 and 20b are CH stretching modes and occur at frequencies above those studied here. Modes 9a and 7a are related to CX in-plane bending and CX stretching, respectively, and occur at frequencies below those studied. Thus, the bands corresponding to modes 1, 6a, 8a, 15, 18b, and 19b were expected to be strongest in SERS and all of these modes appeared with significant intensity in the SERS spectra (see Figure 2A). These results imply that saccharin is adsorbed with the C_2 axes of the o-disubstituted rings approximately perpendicular to the surface and that the increased intensity of the bands near 1600 and 609 cm^{-1} in SERS spectra of the adhesive and of saccharin is related to an orientation effect.

It is interesting to consider the intensity of the band near 786 cm^{-1}. This band, which was assigned to $\nu(12)$, was clearly observed in normal Raman spectra of the salt but not in SERS spectra of saccharin. Under C_{2v}^* symmetry, $\nu(12)$ belongs to the B_2 species and transforms as α_{xy} (16). Considering the selection rules described above, the band near 786 cm^{-1} was expected to be weak in SERS spectra.

No evidence for adsorption of acetylphenylhydrazine (APH) or cumene hydroperoxide (CHP) at the surface of the silver island films was observed in the SERS spectra of the adhesive. Normal Raman spectra of monosubstituted benzene derivatives such as APH and CHP are usually characterized by a very strong band between 990 and 1010 cm^{-1} that is associated with the vibration $\nu(12)$

(17). However, as indicated above, the only band observed near this frequency in SERS spectra of the adhesive was near 1026 cm^{-1} and was attributed to ν(18b) in adsorbed saccharin.

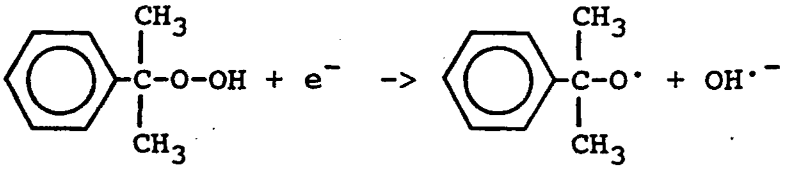
Other results that we have obtained using x-ray photoelectron spectroscopy (XPS) to characterize interphases formed between the same adhesive and metal substrates such as iron, copper, aluminum, and zinc indicate that APH does segregate to the adhesive/metal interphase (18). The difference between the SERS and XPS results may indicate that APH preferentially adsorbs from the adhesive onto iron, copper, aluminum, and zinc but not onto silver. However, it seems more likely that the difference between the SERS and XPS results is related to differences in the techniques. APH and saccharin may both segregate to the interphase but APH may not compete with saccharin for sites on the surface of silver. Since XPS is somewhat less surface sensitive than SERS, APH may be detected in the interphase using XPS but not SERS.

B. SERS spectra of adhesive containing benzoic acid

Benzoic acid was substituted for saccharin and the adhesive was spun onto silver films, and allowed to cure and then the SERS spectra were obtained (15). These spectra were virtually identical to the SERS spectra of benzoic acid and to the normal Raman spectra of the sodium salt of benzoic acid, indicating once again that the strong acids in the adhesive were adsorbed dissociatively onto the metal substrates and that the observed Raman signal was characteristic of the adhesive/substrate interface and not the bulk of the adhesive. No evidence for the adsorption of acetylphenyl-hydrazine (APH) or cumene hydroperoxide (CHP) onto the silver surface was obtained when the adhesive with benzoic acid was cured against silver.

The salts formed at the interface by dissociation of the strong acids may play an important role in the polymerization of the adhesive (15). As indicated earlier, the adhesive considered here is a model anaerobic system that polymerizes rapidly at room temperature by a redox mechanism in the presence of certain metals. The metal ions in the salts are undoubtedly oxidized while the hydroperoxide is reduced to form radicals which

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



(4)

initiate polymerization of the monomer.

Interaction of metal ions with APH may also be an important factor in accelerating the polymerization (15). APH may break down at the metal surface to form radicals which also initiate polymerization. APH may also be oxidized while metal ions are reduced to their original valence state, thus enabling reaction

$$M^{+(n+1)} + e^{-} \rightarrow M^{+n} \qquad (5)$$

4 to be repeated.

C. SERS spectra of pyromellitic diiimide adsorbed on silver

The normal Raman spectrum obtained from pyromellitic diimide (PMDI) is shown in Figure 3. Most of the bands were assigned to vibrations characteristic of the imide groups (19, 20). Remaining bands were assigned to vibrations characteristic of a

2,3,5,6-tetrasubstituted benzene derivative using the Wilson numbering system.

The strong band near 1775 cm^{-1} and the weak band near 1748 cm^{-1} in the normal Raman spectrum were assigned to the "in-phase" and "out-of-phase" stretching modes of carbonyl groups, respectively. The medium intensity bands near 1368 cm^{-1} and 762 cm^{-1} were attributed to the axial stretching mode of the CNC bonds and to the ring breathing mode $\nu(1)$, respectively.

The band near 1633 cm^{-1} was assigned to the tangential ring stretching mode $\nu(8a)$ while the band near 1200 cm^{-1} was assigned to $\nu(7a)$, a CX stretching mode. The band near 659 cm^{-1} was attributed to δ(CNC), a mode involving deformation of the CNC bond angles. Weak bands near 578 and 520 cm^{-1} were related to $\nu(3)$ and $\nu(6b)$, CX in-plane bending and radial stretching vibrations, respectively.

SERS spectra obtained from PMDI films spin coated onto silver island films from 1%, 0.1%, 0.05%, and 0.001% solutions in dimethylformamide are shown in Figure 4. The SERS spectra obtained from PMDI spin-coated onto silver island films from solutions having concentrations of 1%, 0.1%, and 0.05% were virtually identical and independent of the thickness of the films, demonstrating that SERS is a surface-selective effect.

The spectrum shown in Figure 4D was only observed when PMDI films were deposited from solutions having concentrations of approximately 0.001%. Spectra deposited from solutions having higher concentrations always resembled those shown in Figures 4A, 4B, and 4C. Thus the spectrum shown in Figure 4D was considered to be characteristic of a "first layer" of PMDI that was chemisorbed onto silver while the other spectra in Figure 4 were considered to be characteristic of PMDI that was physisorbed.

Moskovits and DiLella also noted a first layer effect in SERS spectra of trans-2-butene (21). A strong band was observed near 1632 cm^{-1} in SERS spectra of trans-2-butene that and assigned to chemisorbed species. A related band due to physisorbed species was observed at somewhat higher frequencies and was approximately 20 times weaker.

The strong band near 1775 cm^{-1} and the medium intensity band near 762 cm^{-1} in normal Raman spectra of PMDI were weak in SERS spectra. Bands near 1368 and 1200 cm^{-1} in the normal Raman spectra were intense in the SERS spectra. Weak bands near 578 and 520 cm^{-1} in normal Raman spectra were weak in the SERS spectra. A band near 690 cm^{-1} which was not observed in the normal Raman spectrum was strong in the SERS spectra.

As noted above, there are several reasons for bands to have different intensities in SERS and normal Raman spectra. Bands which are "normally allowed" for the free molecule may have considerably different intensities in SERS because of orientation effects. Bands which are "normally forbidden" under the symmetry of the free molecule may appear in SERS spectra because of a reduction in symmetry brought about by the formation of surface complexes or because of the contribution of higher order terms to the polarizability.

In the case of PMDI adsorbed onto silver, it was concluded that most differences in relative intensities of bands in normal

Raman and SERS spectra were related to an orientation effect and could be explained by the theory of Moskovits. PMDI belongs to the point group D_{2h} in which α_{zz} belongs to the symmetry species A_g. The strongest lines in the SERS spectra should correspond to species A_g and involve motions that are largely parallel to the twofold axis $C_2(z)$. The second strongest Raman lines should correspond to modes belonging to species B_{2g} or B_{3g} and transforming as α_{xz} and α_{yz}, respectively.

The bands near 1372 and 1202 cm^{-1} in the SERS spectra of PMDI were assigned to an axial CNC stretching mode and to n(7a), a CX stretching mode, respectively. Assuming that PMDI is adsorbed with a vertical conformation in which the molecular rings are perpendicular to the surface and one imide group is attached to the surface (see Figure 5), both of these modes would belong to the same symmetry species as α_{zz} and involve atomic motions that are mostly perpendicular to the surface. The strongest band in the normal Raman spectrum, near 1775 cm^{-1}, was not observed in the SERS spectrum. That band was assigned to a C=O stretching mode belonging to the symmetry species Ag and might be expected to be strong in the SERS spectrum of PMDI. However, for PMDI adsorbed with the orientation shown in Figure 5, the C=O stretching modes are mostly parallel to the surface and the corresponding Raman lines should be weak.

It is extremely interesting to consider the origin of the strong band near 690 cm^{-1} in the SERS spectrum of PMDI. As discussed below, bands were also observed near this frequency in the SERS and normal Raman spectra of phthalimide (PIMH). A band has also been observed near 690 cm^{-1} in normal Raman spectra of succinimide (22). However, no band was observed near 690 cm^{-1} in the normal Raman spectrum of PMDI.

The band near 690 cm^{-1} in the normal Raman spectrum of succinimide has been assigned to a bending vibration of the CCC bond angles belonging to the B_2 symmetry species (22). The corresponding mode for PIMH is ν(18a) in the Wilson notation. PIMH belongs to the point group C_{2v} and ν(18a) is normally allowed for the free molecule. However, ν(18a) is usually found at much lower frequencies in compounds having 2,3;5,6-tetrasubstituted benzene rings (23) and assignment of the band near 690 cm^{-1} in SERS spectra of PMDI to ν(18a) was considered unlikely.

The out-of-plane ring bending vibration ν(4) is expected very near 690 cm^{-1} for PMDI (24). However, this mode belongs to the species B2g for PMDI and transforms the same as α_{xz}. Therefore, it is not expected to be strongly enhanced in the SERS spectra. However, the band near 690 cm^{-1} was strongly enhanced and was clearly observed even when PMDI was adsorbed onto silver island films from solutions having a nominal concentration of only 0.001% and assignment to ν(4) was also considered unlikely.

The most likely assignment of the band near 690 cm^{-1} in the SERS spectra of PMDI is to δ(CNC), the CNC deformation mode, shifted upward from 659 cm^{-1} in normal Raman spectra of PMDI by chemisorption of the imide groups to silver. As noted below, a similar assignment was made for a band observed near 690 cm^{-1} in SERS spectra of phthalimide.

D. SERS from phthalimide adsorbed on silver

The normal Raman spectrum of phthalimide (PIMH) was characterized by strong bands near 1770, 1020, 750, and 560 cm^{-1} which were assigned to the symmetric C=O stretching of the imide carbonyl groups, the CH in-plane-bending mode $\nu(18b)$, the ring breathing mode $\nu(1)$, and the radial ring stretching mode $\nu(6a)$, respectively. Medium intensity bands near 1740, 1620, 1150, and 650 cm^{-1} were assigned to asymmetric stretching of the C=O bonds, the tangential ring stretching mode $\nu(8b)$, the CX in-plane bending mode, and the imide group deformation mode $\delta(CNC)$, respectively.

The SERS spectrum obtained from PIMH spin-coated onto silver island films from a dilute solution in dimethylformamide was very similar to SERS spectra of PMDI in that the strongest band in the normal Raman spectrum, the C=O stretching mode near 1770 cm^{-1}, was not observed in the SERS spectra. Moreover, a strong band appeared near 690 cm^{-1} in the SERS spectra of PIMH that was attributed to $\delta(CNC)$ shifted from near 650 cm^{-1} by chemisorption. It is known that this mode is shifted upward by about 16 cm^{-1} in normal Raman spectra of the potassium salt of PIMH (25). It was concluded that PIMH was also adsorbed onto silver with a vertical conformation similar to that shown in Figure 5 for PMDI.

E. SERS from pyromellitic diimide adsorbed onto graphite

Several experiments were done in which PMDI films were deposited onto highly oriented pyrolytic graphite (HOPG) substrates and silver island films were then evaporated on top of the PMDI films. SERS spectra obtained from these samples did depend on the thickness of the PMDI films. When the PMDI films were relatively thick, the SERS spectra resembled the normal Raman spectra of PMDI. However, when the PMDI films were very thin, the SERS spectra were similar to those obtained from PMDI films deposited onto silver island films (see Figure 6).

Comparing the results shown in Figures 4 and 6, it can be seen that the SERS spectra did not depend on the thickness of the PMDI films when the PMDI films were deposited onto silver island films. However, the SERS spectra did depend on the thickness of the PMDI films when silver island films were deposited onto PMDI films. We consider that these differences are related to an orientation effect. When PMDI films are deposited on a substrate, molecules in the first monolayer have the vertical conformation with one imide group in contact with the surface. PMDI molecules farther away from the substrate have a random orientation. When PMDI films are deposited onto silver substrates, only molecules adjacent to the silver contribute to the SERS. Those molecules always have the configuration shown in Figure 5 regardless of the thickness of the PMDI film and the SERS spectra are independent of the thickness of the PMDI films. When silver island films are deposited on top of PMDI films, once again only molecules adjacent to the silver contribute to the SERS. Those molecules have a random orientation for thick PMDI films but have the vertical configuration for thin PMDI films. Thus, in that case, the SERS spectra depend on the thickness of the PMDI films.

IV. Conclusions

SERS can be used as a non-destructive technique for characterizing the interface between metals and polymers as long as the thickness of the polymer film is not so great that normal Raman scattering by the bulk of the film becomes comparable in intensity to the SERS from the interface. The technique can be used to determine mechanisms of adsorption and the orientation of adsorbed species.

SERS spectra obtained from a model acrylic adhesive consisting of the monomer triethylene glycol dimethacrylate and a curing system containing saccharin, acetylphenylhydrazine, and cumene hydroperoxide were similar to SERS spectra of saccharin and to normal Raman spectra of the sodium salt of saccharin. These results demonstrate that saccharin segregated to the interface and adsorbed onto the silver substrate dissociatively to form a metal salt. The salts are important factors in the curing reaction of the adhesive since metal ions catalyze decomposition of the hydroperoxide to form radicals that initiate polymerization of the monomer and may also catalyze formation of radicals from APH.

SERS spectra obtained from pyromellitic diimide adsorbed onto silver island films were much different than normal Raman spectra of PMDI due to orientation effects. PMDI was adsorbed onto silver island films through the imide groups with a vertical conformation in which the two-fold symmetry axes passing through the nitrogen atoms were perpendicualr to the silver surface. The SERS spectra were mostly independent of the thickness of the PMDI films, again indicating that SERS is an interface rather than bulk effect.

SERS spectra obtained using silver island films deposited onto PMDI films adsorbed onto graphite substrates did depend on the thickness of the PMDI films. Spectra obtained from thick PMDI films were similar to the normal Raman spectra of PMDI. However, SERS spectra obtained from thin films of PMDI supported by graphite were similar to those obtained from PMDI adsorbed onto silver island films. It was concluded that PMDI was adsorbed with a two-phase structure in which molecules adjacent to the substrate were preferentially oriented perpendicular to the surface while those farther away had random orientation.

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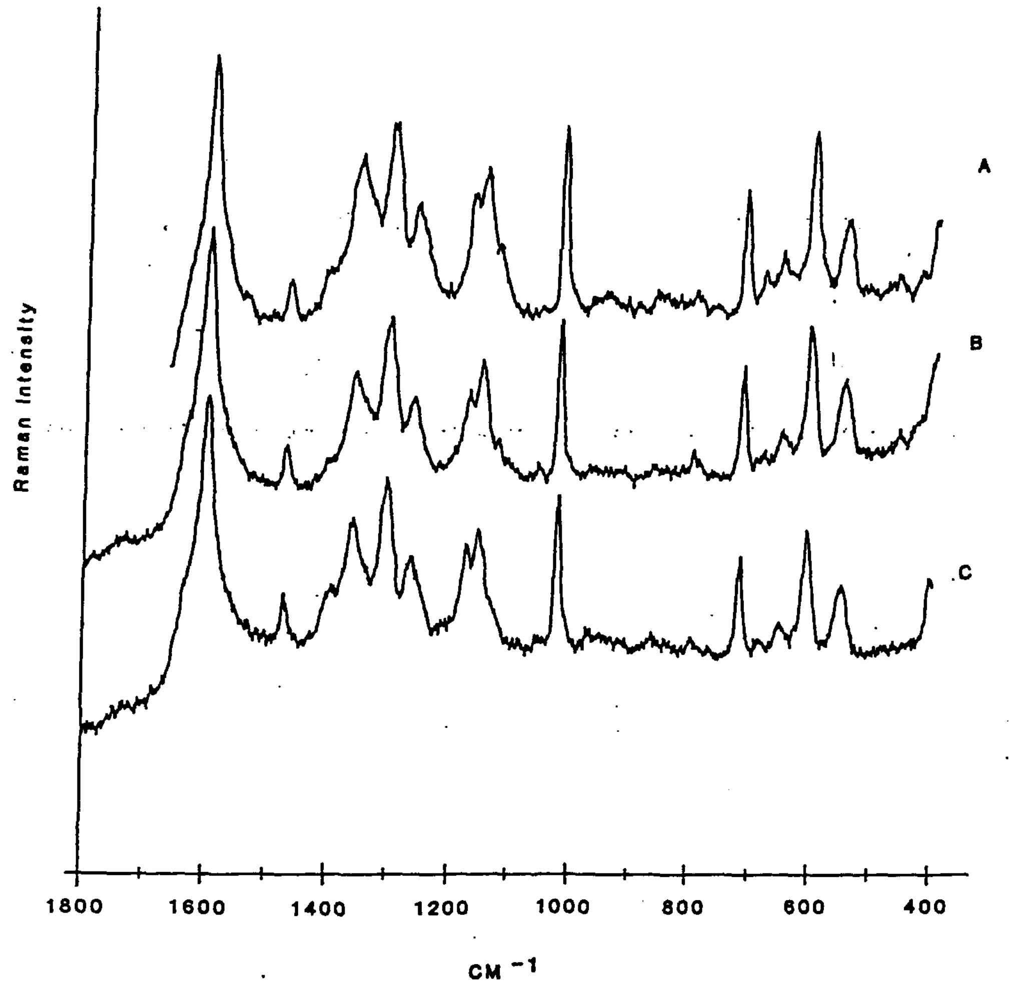

Figure 1. SERS spectra obtained when the acrylic adhesive was spin-coated onto silver island films from (A) - 1% and (B) - 5% solutions in acetone and (C) - from the bulk. The scale factor was 5x10^3 counts/sec and the laser power was 100 mW. Adapted with permission from reference 15.

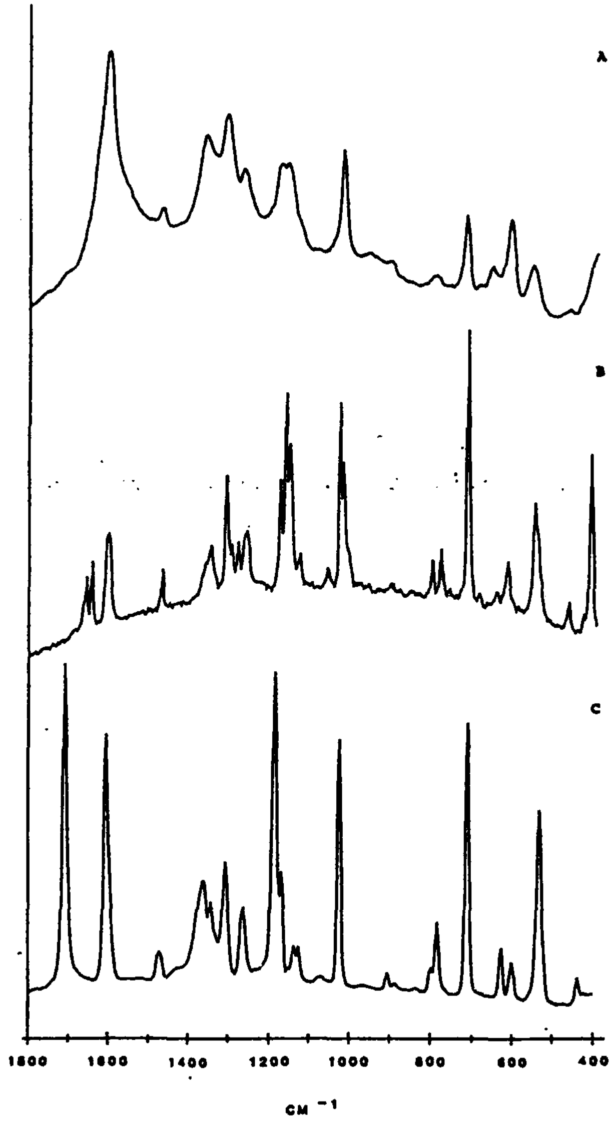

Figure 2. (A) - SERS spectrum from saccharin spin-coated onto a silver island film from a 0.1% acetone solution, (B) - normal Raman spectrum of the sodium salt of saccharin, and (C) - normal Raman spectrum of saccharin. Adapted with permission from reference 15.

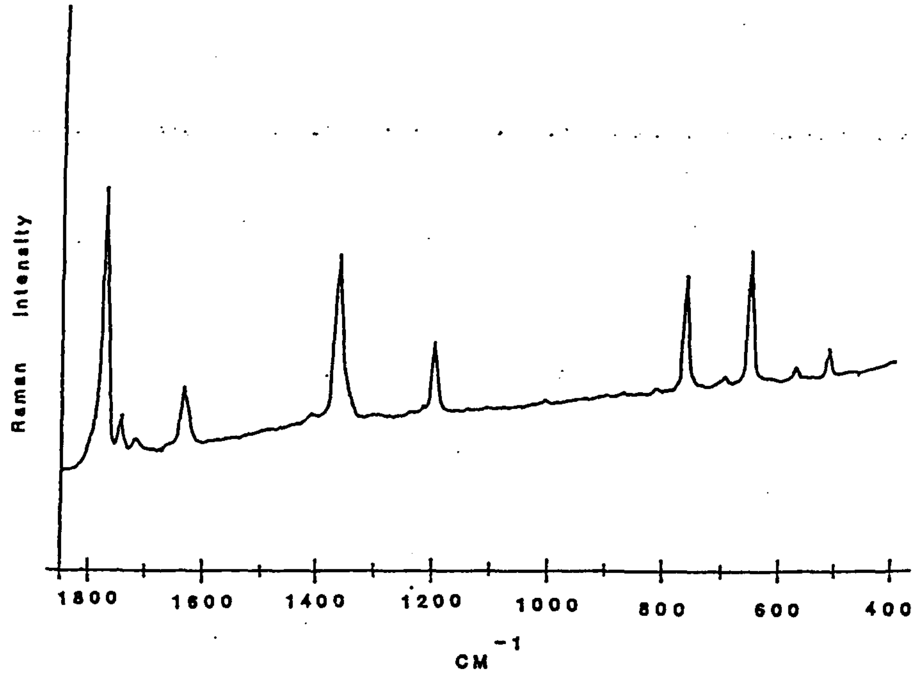

Figure 3. Normal Raman spectrum of pyromellitic diimde (PMDI).

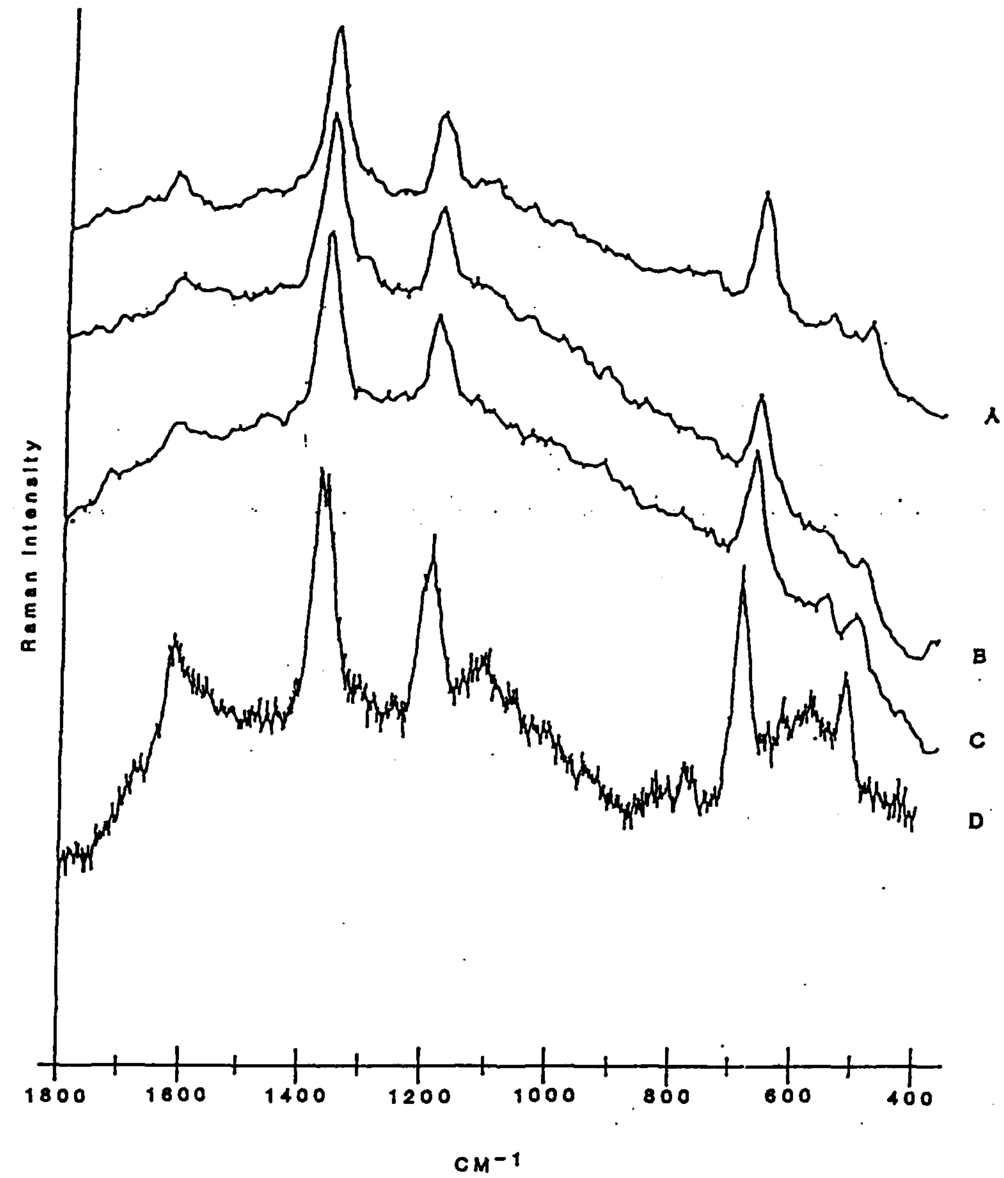

Figure 4. Surface-enhanced Raman spectra obtained from thin films of PMDI spin-coated onto silver island films from (A)-1%, (B)-0.1%, (C)-0.05%, and (D)-0.001% solutions.

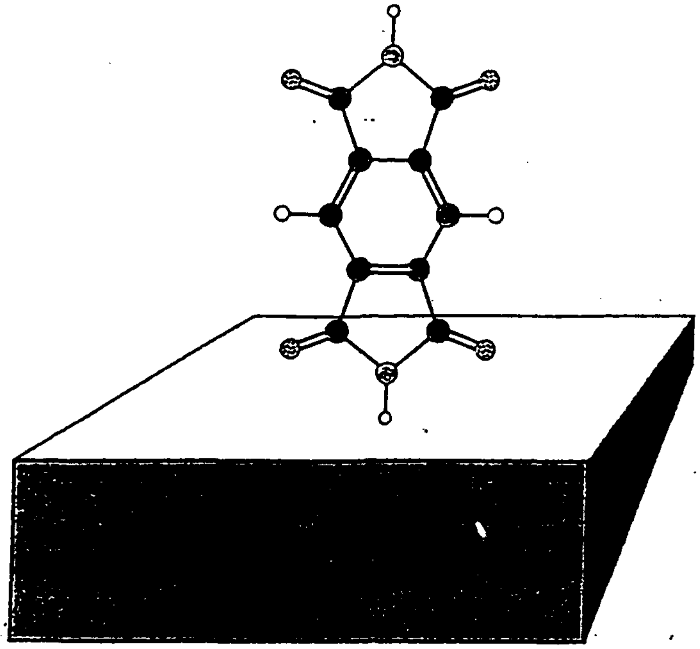

Figure 5. Vertical conformation for adsorbed PMDI molecules.

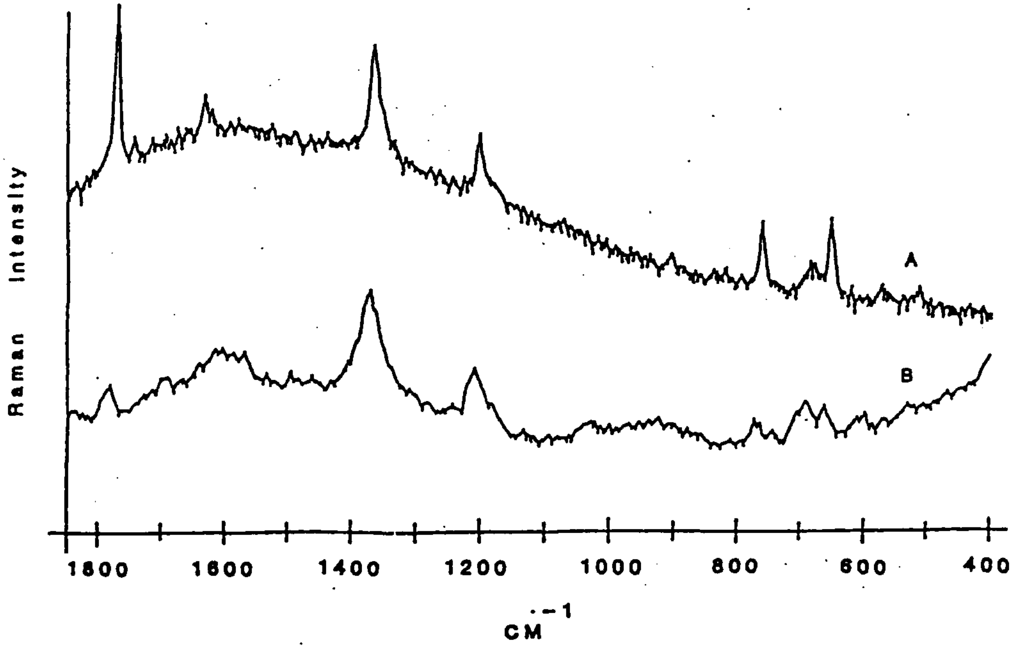

Figure 6. SERS spectra obtained from PMDI films deposited onto highly oriented pyrolytic graphite (HOPG) from (A)-2% and (B)-0.01% solutions and then overcoated with silver island films.

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