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# Characterization of Model Polyimide/Silver Interphases Using Surface-Enhanced Raman Scattering

by

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

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University of Cincinnati
Cincinnati, OH 45221-0012

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Surface-enhanced Raman scattering (SERS) was used to investigate the adsorption of model compounds for polyimides onto silver island films and onto highly oriented pyrolytic graphite (HOPG). SERS spectra of pyromellitic diimide (PMDI) adsorbed onto silver island films were mostly independent of the thickness of the PMDI films, confirming that SERS is an interfacial rather than bulk effect and that SERS can be used to examine the interface between an adsorbed film and a metal substrate without interference from normal Raman scattering by the bulk of the film. Differences in the relative intensities of several bands in the normal Raman and SERS spectra of PMDI adsorbed onto silver island films were related to orientation effects. It was concluded that most molecules were physisorbed with a vertical configuration in which the plane of the molecules was perpendicular to the surface and one imide group was adjacent to the surface. However, a strong band near

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690 $cm^{-1}$ in the SERS spectra was assigned to PMDI chemisorbed with a vertical configuration. Similar conclusions were reached for phthalimide (PIMH) adsorbed onto silver island films. When PMDI was deposited onto an HOPG substrate and silver island films were deposited on top of the PMDI, the SERS spectra did depend on the thickness of the PMDI films. For thick PMDI films, the SERS spectra were similar to normal Raman spectra of bulk PMDI but for thin films, the SERS spectra were similar to those obtained from PMDI deposited onto silver. It was concluded that the molecules in thick films of PMDI were mostly randomly oriented but those closest to the substrate had a vertical configuration. SERS spectra of N-phenyl phthalimide and N, N-diphenyl pyromellitic diimide adsorbed onto silver were very similar to the normal Raman spectra. It was concluded that both of these compounds were adsorbed edge-on with one (N-phenyl phthalimide) or two (N, N-diphenyl pyromellitic diimide) carbonyl groups adjacent to the surface.

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W. H. Tsai, J. T. Young, F. J. Boerio, and P. P. Hong
Department of Materials Science
and Engineering
University of Cincinnati
Cincinnati, Ohio 45221

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# ABSTRACT

Surface-enhanced Raman scattering (SERS) was used to investigate the adsorption of model compounds for polyimides onto silver island films and onto highly oriented pyrolytic graphite (HOPG). SERS spectra of pyromellitic diimide (PMDI) adsorbed onto silver island films were mostly independent of the thickness of the PMDI films, confirming that SERS is an interfacial rather than bulk effect and that SERS can be used to examine the interface between an adsorbed film and a metal substrate without interference from normal Raman scattering by the bulk of the film. Differences in the relative intensities of several bands in the normal Raman and SERS spectra of PMDI adsorbed onto silver island films were related to orientation effects. It was concluded that most molecules were physisorbed with a vertical configuration in which the plane of the molecules was perpendicular to the surface and one imide group was adjacent to the surface. However, a strong band near 690 $cm^{-1}$ in the SERS spectra was assigned to PMDI chemisorbed with a vertical configuration. Similar conclusions were reached for phthalimide (PIMH) adsorbed onto silver island films. When PMDI was deposited onto an HOPG substrate and silver island films were deposited on top of the PMDI, the SERS spectra did depend on the thickness of the PMDI films. For thick PMDI films, the SERS spectra were similar to normal Raman spectra of bulk PMDI but for thin films, the SERS spectra were similar to those obtained from PMDI deposited onto silver. It was concluded that the molecules in thick films of PMDI were mostly randomly oriented but those closest to the substrate had a vertical configuration. SERS spectra of N-phenyl phthalimide and N, N-diphenyl pyromellitic diimide adsorbed onto silver were very similar to the normal Raman spectra. It was concluded that both of these compounds were adsorbed edge-on with one (N-phenyl phthalimide) or two (N, N-diphenyl pyromellitic diimide) carbonyl groups 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 metals such as silver, copper, and gold is enhanced by as much as $10^6$ relative to the normal cross section of the free molecules. Numerous theories of SERS have been proposed. However, it now appears that most of the enhancement can be explained by two mechanisms. One is associated with electromagnetic resonances within a metallic substrate which enhance the electric field at the surface (1). This model predicts a relatively long-range (several adsorbed monolayers) enhancement. The other mechanism is related to distortion of the molecular polarizability by the formation of charge-transfer complexes (1). This mechanism is relatively short range and is operative only for chemisorbed molecules.

Numerous reports have appeared indicating that SERS may be used as a probe for polymer/metal interfaces. Allara, Murray, and Bodoff investigated SERS from poly (p-nitrostyrene) (PPNS) using silver "overlayers" and polystyrene (PS) using silver "underlayers" (2). In one case, PPNS films of varying thickness were spin-coated onto aluminum substrates and silver island films approximately 200 A thick were deposited on top of the polymer films. In the other case, silver island films approximately 100 A in thickness were deposited onto glass slides and PS films of varying thickness were spin-coated onto the silver surfaces. In both cases, the SERS intensity initially increased as a function of polymer film thickness and then became saturated at a certain thickness which depended on the morphological features of the silver island films. When the silver films were nearly continuous, enhanced scattering was observed from several hundred angstroms into the polymer films. However, enhanced Raman scattering was observed from only the first few tens of angstroms of polymer at the silver surface when the silver island films had sharp features. It was suggested that SERS might be useful for depth profiling the surface regions of polymer films.

Venkatachalam et al (3) investigated SERS from bilayers of polystyrene (PS), diglycidyl ether of bisphenol-A (DGEBA), poly (4-vinyl pyridine) (PVP), and poly (styrene sulfonate) (PSS). Samples were prepared by spin-coating films of PS, DGEBA, or PVP were spun onto silver island films from dilute solutions and then overcoating them with films of PSS. It was found that SERS could be observed from both layers of polymer when the first layer was spun from a relatively dilute solution. Otherwise, SERS was only observed from the first layer (PS, DGEBA, or PVP) even though the PSS films were strong Raman scatters. These results confirmed that SERS was an interface effect and that the enhancement extended no more than about a hundred angstroms from the silver surface. It was concluded that SERS could be used for the non-destructive characterization of interfaces between polymer films and metal substrates without interference from normal Raman scattering by the bulk of the polymer as long as the thickness of the polymer films was less than about a thousand angstroms.

Boerio et al (4) investigated SERS from poly ($\alpha$-methylstyrene) (PMS) spin-coated onto silver island films from methyl ethyl ketone (MEK) solutions having various concentrations. The intensity of the bands near 722, 1012, 1042, and 1613 $cm^{-1}$ was approximately constant even though the thickness of the PMS films varied from about 300 to 2000 angstroms, again demonstrating that SERS was an interface rather than bulk effect.

Several authors have investigated the selection rules for Raman scattering by molecules adsorbed onto metal substrates. Moskovits developed a theory that was based strictly on electromagnetic effects (5). 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 $\alpha_{zz}$ where z is the coordinate perpendicular to the metal surface. The next most intense lines should correspond to modes transforming the same as $\alpha_{xz}$ and $\alpha_{yz}$. The weakest lines should correspond to modes transforming as $\alpha_{xy}$, $\alpha_{xx}$, and $\alpha_{yy}$. Modes transforming as $\alpha_{zz}$ 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. 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 (6).

These predictions have been investigated by several groups and used to determine the orientation of adsorbed molecules. 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 (6). The spectra were adequately 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 (6). 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. $\alpha_{zz}$ 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 which were attributed to the molecular orientation. The intensity of the band assigned to mode $\nu(8a)$ increased relative to that of the band assigned to mode $\nu(1)$ 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 $\pi$-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.

The 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 to become 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).

Adhesion of polyimides to metals and graphite fibers is important in the areas of electronics and composites. As a result, it is essential to determine the molecular structures of polyimide/metal and polyimide/fiber interfaces. The primary purpose of this paper is to report results we have obtained using SERS to determine the molecular structure of interphases between phthalimide (PIMH), pyromellitic diimide (PMDI), N-phenyl PIMH, and N, N-diphenyl PMDI and silver island films and between PMDI and highly oriented pyrolytic graphite (HOPG). PIMH, PMDI, N-phenyl PIMH, and N, N-diphenyl PMDI were considered as model compounds for PMDA/ODA polyimides. Silver island films were used as a model metal and HOPG was viewed as a model for graphite fibers.

## II. Experimental

Phthalimide (PIMH) and pyromellitic diimide (PMDI) were obtained from Aldrich. N-phenyl phthalimide (N-phenyl PIMH) was obtained from Pfaltz and Bauer. N,N-diphenyl pyromellitic diimide (N, N-diphenyl PMDI) was synthesized as follows. Pyromellitic dianhydride (PMDA, 99.0%) and aniline (99.5%) obtained from Aldrich were added into N-methylpyrrolidone (NMP) in a 2:1 mole ratio to make a 10% solution by weight. The solution was heated to 175°C under flowing $N_2$ for 1.5 hours during which time pale yellow particles precipitated. At the end of the reaction, the precipitate was washed with DMF several times, recrystallized from a DMF-methanol mixed solvent, and dried under vacuum.

Samples were prepared for SERS investigations as described below. Glass slides were immersed in 0.1N NaOH and in 0.1N HCl aqueous solutions for one hour. The slides were then rinsed in distilled-deionized water, blown dry with nitrogen, cleaned ultrasonically in absolute ethanol several times, and blown dry with nitrogen again.

The glass slides were placed in a vacuum chamber which was purged with nitrogen and pumped down to $10^{-6}$ Torr using sorption, sublimation, and ion pumps. Silver wire was wrapped around a tungsten filament which was slowly heated resistively to evaporate island films onto the glass and HOPG substrates at a rate of about 1 A/sec. A quartz crystal oscillator thickness monitor was used to control the thickness of the island films at about 40 A.

Thin films of PIMH, PMDI, and N-phenyl PIMH were deposited on the silver island films by spin-coating from solutions in dimethylformamide. The solutions were filtered through activated charcoal before use to eliminate fluorescent impurities. Films of N, N diphenyl PMDI were deposited by placing a few drops of a dilute solution in hot DMF onto the silver substrates and allowing the solvent to evaporate.

HOPG substrates (Union Carbide) were cleaned ultrasonically in acetone and then blown dry with nitrogen. PMDI films were deposited by dipping the cleaned substrates into dilute solutions in DMF. The samples were then placed in the vacuum chamber and silver was evaporated as described above.

SERS spectra were obtained using a spectrometer equipped with a Spex 1401 double monochromator, an ITT FW130 photomultiplier tube, Harshaw photon counting electronics, and a Spectra-Physics Model 165 argon-ion laser. The slit settings of the monochromator provided a spectral resolution of 10 $cm^{-1}$ for the SERS spectra. The green line of the laser (5145 angstroms in wavelength) was incident on the sample at an angle of about $65^{o}$ relative to the normal of the sample surface for SERS experiments and was s-polarized. Scattered light was collected using an f/0.95 collection lens and focused onto the entrance slits of the monochromator. Spectra were obtained using a scan speed of 50

$cm^{-1}$ per minute and time constant of either 2 or 10 seconds. Plasma lines were removed from the spectra by the placement of a narrow-bandpass filter between the laser and sample.

Normal Raman spectra were obtained from a small amount of powdered sample supported in a glass capillary tube using the instrument described above and techniques which have been described elsewhere (8). All of the instrumental parameters were the same as used for the SERS spectra except that the slits were set for a spectral width of 5 $cm^{-1}$.

The thickness of the PMDI and PIMH films deposited on the silver island films was determined by ellipsometry. Thick (several hundred angstroms) films of silver were evaporated onto glass slides. Films of PMDI or PIMH were spun onto the silver mirrors from the same solutions and at the same speeds as were used to prepare the SERS samples. The thickness of the films was measured using a Rudolph Research Model 436 ellipsometer to examine the silver substrates before and after deposition of the organic films.

Similar techniques were used to obtain reflection-absorption infrared spectra of PMDI films on silver substrates. Thick films of silver were evaporated onto glass slides and films of PMDI were spin-coated onto the silver. Infrared spectra of the PMDI films were obtained using a Perkin-Elmer Model 1800 Fourier-transform infrared (FTIR) spectrophotometer and external reflection accessories provided by Harrick Scientific Co. Transmission infrared spectra of PMDI were obtained using the same spectrophotometer. Samples were prepared by mixing a small amount of PMDI powder with potassium bromide powder and then pressing the mixture into a clear pellet under high pressure.

## III. Results and Discussion

### A. *Phthalimide*

The normal Raman spectrum of phthalimide (PIMH) is shown in Figure 1 and the observed bands are summarized in Table I. Bands observed in the infrared spectra of PIMH are also summarized in Table I. Most of the observed bands were assigned to vibrations characteristic of the imide group (9, 10). The remaining bands were assigned to vibrations of a 2,3-disubstituted benzene derivative using the numbering system that was introduced by Wilson (11) and summarized by Varsanyi (12).

The strongest bands in the normal Raman spectra, near 1770, 1020, 750, and 560 $cm^{-1}$, 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 CH 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 is shown in Figure 2 and the observed bands are also summarized in Table I. Some interesting differences were observed between the normal Raman and SERS spectra of PIMH. The C=O stretching mode near 1770 $cm^{-1}$, which was the strongest band in the normal Raman spectrum, was quite weak in the SERS spectra. Moreover, a strong band appeared near 690 $cm^{-1}$ in the SERS spectra of PIMH but only a weak band was observed near that frequency in normal Raman spectra of PIMH.

As discussed 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.

There are no normally forbidden bands in Raman spectra of PIMH since PIMH has $C_{2v}$ symmetry and vibrational modes belonging to all symmetry species are active. Differences between the normal Raman and SERS spectra of PIMH were related to orientation effects.

Two orientations of PIMH adsorbed onto silver are consistent with the observed spectra. In one, PIMH is adsorbed end-on, with the imide group adjacent to the surface. In the other, the molecules are adsorbed flat. Either orientation is consistent with the low intensity observed for the imide C=O stretching mode near 1770 $cm^{-1}$. The assignment of the strong line near 690 $cm^{-1}$ in the SERS spectra is crucial in determining the orientation.

We have considered two possible assignments for the band near 690 $cm^{-1}$. One is to $\nu(4)$, an out-of-plane bending mode of the benzene rings. The other is to the imide deformation mode, $\delta$(CNC).

$\nu$(4) is usually assigned to a weak band between 685 and 735 $cm^{-1}$ in Raman spectra of o-disubstituted benzene compounds (13). As shown in Table I, this mode was assigned to a weak band near 690 $cm^{-1}$ in normal Raman spectra of PIMH. However, it is very unusual for the band corresponding to $\nu$(4) to be as strong as the band near 690 $cm^{-1}$ in the SERS spectra of PIMH. For example, Moskovits (7) has observed a weak band corresponding to $\nu$(4) near 744 $cm^{-1}$ in SERS spectra of pyrazine adsorbed onto silver with a flat configuration.

A band attributed to the $\delta$(CNC) mode is observed near 650 $cm^{-1}$ in normal Raman spectra of PIMH (14). This band is shifted upward by about 16 $cm^{-1}$ in spectra of the potassium salt (15). It is possible that the band near 690 $cm^{-1}$ in SERS spectra of PIMH is related to the $\delta$(CNC) mode shifted upward by interaction of the imide group with the silver substrate. Our tentative conclusion is that the band near 690 $cm^{-1}$ is related to $\delta$(CNC) shifted by interaction of PIMH through the imide group and that PIMH is adsorbed end-on with the imide group adjacent to the substrate.

## *B. Pyromellitic Diimide*

The normal Raman spectrum obtained from PMDI is shown in Figure 3 and the observed bands are summarized in Table II. For convenience, the bands observed in the infrared spectrum of PMDI are also summarized in Table II. Most of the observed bands were assigned to vibrations characteristic of the imide group of PMDI.

The remaining bands were assigned to vibrations 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 $\delta(CNC)$, 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.

The infrared spectrum was characterized by strong bands near 1772 and 1720 $cm^{-1}$, bands with medium intensity near 3200, 1379, 1307, 1156, 1062, and 728 $cm^{-1}$, and weak bands near 1567, 1470, 775, 637, and 560 $cm^{-1}$. The prominent bands near 1772 and 1720 $cm^{-1}$ were assigned to the "in-phase" and the "out-of-phase" stretching modes of carbonyl groups. Medium intensity bands near 1379 and 1062 $cm^{-1}$ were related to axial and transverse stretching modes of the CNC bond (9). The medium intensity band near 728 $cm^{-1}$ was assigned to the CNC out-of-plane bending mode.

Other bands in the infrared spectrum were related to the vibrations of the benzene ring. Medium intensity bands near 1307 and 1156 $cm^{-1}$ were assigned to $\nu(14)$, a ring stretching mode, and to $\nu(13)$, a mode related to the stretching vibration between the rings and the substituents, respectively. Weak bands due to $\nu(19b)$ and $\nu(19a)$, ring stretching modes, were found near 1567 and 1470 $cm^{-1}$, respectively. Other bands near 775, 637, and 560 $cm^{-1}$ were assigned to $\nu(20b)$, a mode involving the stretching vibration between the rings and the substituents, to $\nu(12)$, a radial skeletal vibration, and to $\nu(16a)$, an out-of-plane skeletal vibration, respectively (12).

SERS spectra obtained from PMDI films spin coated onto silver island films from 1%, 0.1%, 0.05%, and 0.001% solutions are shown in Figure 4. The observed bands are also summarized in Table II. 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. The other spectra in Figure 4 contained features characteristic of the first layer and a few multilayers.

Moskovits and DiLella have also noted a first layer effect in SERS spectra of trans-2-butene (16). They observed a strong band near 1632 cm$^{-1}$ in SERS spectra of trans-2-butene that was 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. The band near 690 cm$^{-1}$ was not observed in the normal Raman spectrum but was strong in the SERS spectra.

As indicated above, there are several reasons for bands to have significantly different intensities in normal Raman and SERS spectra. 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 $\alpha_{zz}$ 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 $\alpha_{xz}$ and $\alpha_{yz}$, 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 $\nu(7a)$, a CX stretching mode, respectively. Assuming that PMDI is adsorbed end-on with a vertical configuration in which the molecular rings are perpendicular to the surface and one imide group is attached to the surface, both of these modes would belong to the same symmetry species as $\alpha_{zz}$ 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 end-on, the C=O stretching modes are mostly parallel to the surface and the corresponding Raman lines should be weak.

The out-of-plane ring bending vibration $\nu(4)$ is expected very near 690 $cm^{-1}$ for PMDI (17). This mode belongs to the species B2g for PMDI and transforms the same as $\alpha_{xz}$. 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 $\nu(4)$ was considered unlikely.

The most likely assignment of the band near 690 $cm^{-1}$ in the SERS spectra of PMDI is to $\delta$(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 above, a similar assignment was made for a band observed near 690 $cm^{-1}$ in SERS spectra of phthalimide.

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 (see Figure 5). 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.

Comparing the spectra shown in Figures 4 and 5, 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 also 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 vertical configuration 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.

Reflection-absorption infrared (RAIR) spectra were also obtained from PMDI films deposited onto thick silver substrates from 1%, 0.1%, and 0.01% solutions in DMF (see Figure 6). The observed bands are also summarized in Table II. The thickness of the PMDI films deposited from 1%, 0.1%, and 0.01% solutions was about 50, 22, and 9 angstroms, respectively, as determined by ellipsometry. RAIR spectra of PMDI films spin-coated onto silver island films from 1% and 0.1% solutions were very similar in relative intensity (see Figures 6A and 6B). However, significant differences were observed from the RAIR spectrum of PMDI films deposited onto silver films from the 0.01% solution (see Figure 6C). Only two characteristic bands of PMDI were observed near 1383 and 1311 $cm^{-1}$ in the spectrum shown in Figure 6C. These bands were assigned to the axial stretching mode of the CNC bond and the ring stretching mode $\nu(14)$, respectively.

The results obtained from infrared spectroscopy were consistent with those obtained from SERS showing that the orientation of the molecules in adsorbed PMDI films depended on the film thickness. For relatively thick films, the spectra were dominated by absorption due to randomly oriented molecules and were similar to the bulk spectra of PMDI. However, for thin films, the spectra were determined by the orientation of the molecules adjacent to the substrate.

If the molecules in the films have a preferred orientation, absorption bands corresponding to vibrational modes involving atomic motions that are mostly perpendicular to the substrate surface are expected to be especially strong in RAIR spectra. For PMDI adsorbed end-on with the vertical configuration, the bands near 1383 and 1311 $cm^{-1}$ are expected to be strong since they are assigned to the axial CNC stretching mode and to $\nu(14)$, respectively, and would involve atomic motions that are mostly perpendicular to the surface.

### *C. N-phenyl Phthalimide*

N-phenyl PIMH contains two benzene rings (o-disubstituted and monosubstituted). Some workers have assumed these to be coplanar (9). In that case, there are four symmetry elements, including the identity, a two-fold rotational axis, and two planes of reflection, and the point group is C2v. Others have assumed that the rings are rotated about the CN bond joining them (18,19). In that case, there are only two symmetry elements (two-fold axis and identity) and the point group is C2. We have assumed that the rings are coplanar but that assumption does not strongly affect interpretation of the spectra.

The normal Raman spectrum of N-phenyl PIMH is shown in Figure 7. The observed bands, along with those observed in the infrared spectra, are summarized in Table III. The infrared and Raman spectra were dominated by bands due to the characteristic vibrations of the imide groups. Most bands related to modes of the benzene rings were relatively weak.

The SERS spectrum of N-phenyl PIMH spin-coated onto a silver island film from a 1.0% solution in DMF is shown in Figure 8. When the normal Raman and SERS spectra were compared, it was evident that no significant band shifts or new bands were observed. The most significant differences between the normal Raman and SERS spectra of PIMPh were associated with the relative band intensities.

A medium intensity band near 1785 $cm^{-1}$ in the normal Raman spectrum was assigned to the C=O stretching mode of the imide group. The corresponding band in the SERS spectrum was relatively strong. A strong band near 1395 $cm^{-1}$ in the Raman spectrum was associated with the axial C-N-C stretching mode (imide II) involving atomic motion mostly parallel to the twofold symmetry axis. The corresponding band in the SERS spectra was relatively weak. A medium intensity band near 1117 $cm^{-1}$ in the normal Raman spectrum was associated with the transverse C-N-C stretching mode (imide III) and was relatively strong in SERS spectra. Strong bands near 718 and 1611 $cm^{-1}$ in the Raman spectrum were assigned to modes $\nu(1)$-$C_6H_4$ and $\nu(8a)$-$C_6H_5$, respectively, belonging to the $A_1$ symmetry species of the point group $C_{2v}$. The corresponding bands were observed near 720 and 1612 $cm^{-1}$ in SERS spectra and were relatively strong. Bands near 1022 and 1024 $cm^{-1}$ in the Raman spectrum were assigned to modes $\nu(18a)$-$C_6H_5$ and $\nu(18b)$-$C_6H_4$ belonging to the $B_2$ and $A_1$ species, respectively. These bands combined to form a relatively strong band in the SERS spectra.

According to the surface selection rules, the strongest Raman lines should be observed for vibrations belonging to the same symmetry species as $\alpha_{zz}$, where z is the direction perpendicular to the surface (5). Vibrations involving the motions directed normal to the surface may be especially intense in SERS spectrum. The second strongest Raman lines should belong to the same symmetry species as $\alpha_{xz}$ and $\alpha_{yz}$ (5).

If N-phenyl PIMH molecules were adsorbed with the two-fold axes parallel to the z direction, modes such as $\nu(1)$-$C_6H_4$ and the axial C-N-C stretching mode which belong to the $A_1$ symmetry species and involve motions that are largely parallel to the z direction, should be strongest. However, that is not what was observed. The axial C-N-C stretching mode is actually relatively weak in SERS compared to normal Raman spectra.

The most likely preferred orientation seems to be with the molecules adsorbed edge-on with the two-fold axes parallel to the surface. In that case, the surface selection rule predicts that modes such as the C=O and transverse C-N-C stretching modes should be relatively strong and that is what is observed.

Further evidence that N-phenyl PIMH was adsorbed edge-on with the two-fold symmetry axes parallel to the surface was obtained from the RAIR spectra of N-phenyl PIMH spun onto silver surfaces from 1, 0.1 and 0.01% solutions in DMF (see Figure 9). Significant differences in relative intensity were observed as the thickness of the N-phenyl PIMH films decreased. The band near 1701 $cm^{-1}$ assigned to the C=O stretching mode became stronger as the films became thinner. On the other hand, the band near 1386 $cm^{-1}$ assigned to C-N-C axial stretching mode gradually became less intense as the film thickness decreased. For the thinnest films, only one band near 1701 $cm^{-1}$ was strongly observed, indicating that the transition moment for the C=O stretching mode was directed normal to the silver surface, whereas that for the C-N-C axial stretching was not. These results are consistent with those from SERS.

### *D. N, N - Diphenyl Pyromellitic Diimide*

The normal Raman spectrum of N, N-diphenyl PMDI is shown in Figure 10 and the observed bands, along with those observed in the infrared spectra are summarized in Table IV. Both spectra were dominated by bands due to the characteristic vibrations of the imide groups. Other bands associated with the 2,3,5,6-tetrasubstituted and monosubstituted benzene rings were assigned using Wilson's numbering system.

Figure 11 shows the SERS spectrum of N, N-diphenyl PMDI deposited onto a silver island film from a 0.05% solution in hot DMF. When the normal Raman and SERS spectra were compared, the only differences observed were associated with the relative intensities of some bands. As was the case with N-phenyl PIMH, these differences were most likely due to the orientation effect of N, N-diphenyl PMDI adsorbed onto the silver surface.

For N, N-diphenyl PMDI molecules adsorbed edge-on with two carbonyl groups in contact with the surface, $\alpha_{zz}$ belongs to species $A_g$. The strongest Raman lines should correspond to modes belonging to species $A_g$ and involving motions that are largely parallel to the z axis or perpendicular to the surface. The second strongest Raman lines should belong to $B_{2g}$ or $B_{3g}$ modes which correspond to $\alpha_{xz}$ and $\alpha_{yz}$ symmetry species, respectively.

The band near 740 $cm^{-1}$ in the normal Raman spectrum was assigned to $\nu(1)$-$C_6H_2$, the symmetrical ring breathing mode. The band near 1801 $cm^{-1}$ was associated with the stretching mode of the carbonyl group. Two other bands near 1609 and 1008 $cm^{-1}$ were assigned to modes $\nu(8a)$ and $\nu(18a)$ of the mono-substituted benzene rings. These bands all belong to the $A_g$ symmetry species of the point group D2h and involve atomic motions mostly perpendicular to the surface if N, N-diphenyl PMDI is adsorbed edge-on through the carbonyl groups. On the other hand, the band near 1420 $cm^{-1}$ in the normal Raman spectrum was attributed to the axial C-N-C stretching mode. This vibration would not involve atomic motions perpendicular to the surface if N, N-diphenyl PMDI was adsorbed through the carbonyl groups with an edge-on configuration. As a result, the bands near 1801, 1609, 1008, and 740 $cm^{-1}$ in the normal Raman spectrum should all appear strongly in the SERS spectra and that is exactly what was observed. The band near 1420 $cm^{-1}$ in the normal Raman spectrum was expected to be weak in the SERS spectrum and that is also what was observed.

RAIR experiments were carried out to provide complementary information. RAIR spectra of DPPMDI deposited onto silver films from 0.05, 0.005, and 0.001% solutions in DMF are shown in Figure 12. As the thickness of the films was decreased, the band near 1723 $cm^{-1}$, which was assigned to the stretching mode of the carbonyl groups, became considerably stronger relative to the band near 1401 $cm^{-1}$, which was assigned to the C-N-C axial stretching mode. This is exactly the behavior expected if the molecules nearest to the silver surface were adsorbed edge-on with two carbonyl groups adjacent to the surface. In that case, the transition moment for the carbonyl stretching mode would be perpendicular to the surface, resulting in relatively high intensity for that mode. The transition moment for the axial C-N-C stretching mode would be parallel to the surface, resulting in relatively low intensity. Results obtained from infrared spectroscopy were thus consistent with those obtained from SERS.

The results obtained here indicate that PIMH and PMDI are adsorbed end-on with one imide group adjacent to the surface. N-phenyl PIMH and N, N-diphenyl PMDI are adsorbed edge-on with one (N-phenyl PIMH) or two (N, N-diphenyl PMDI) carbonyl groups adjacent to the surface. Debe (20) observed orientation effects in infrared spectra of perylene red adsorbed onto aluminum that were somewhat similar to the orientation effects observed here. At the interface, one third of the molecules were standing edge-on and two thirds were standing end-on but none were flat. Farther from the substrate surface, the molecules had a random orientation.

Ramsier and Henriksen, however, used inelastic electron tunneling spectroscopy (IETS) to conclude that PIMH was adsorbed flat (21). The reasons for the discrepancy between their conclusions and ours are not known. However, it should be noted that the conclusions of Ramsier and Henriksen were based solely on IETS whereas those reported here were based on a combination of SERS and RAIR.

## IV. Conclusions

Surface-enhanced Raman scattering (SERS) has been used to determine the molecular structure of interphases between model compounds for polyimides and silver island films. SERS spectra obtained from pyromellitic diimide (PMDI) films adsorbed onto silver were mostly independent of the thickness of the PMDI films, indicating that SERS is an interface rather than bulk effect. Phthalimide (PIMH) and PMDI were adsorbed onto silver end-on with one imide group adjacent to the surface. N-phenyl PIMH and N, N-diphenyl PMDI were adsorbed edge-on with one or two carbonyl groups adjacent to the surface.

SERS experiments were also carried out using silver island films evaporated onto PMDI films supported by HOPG. In that case, the SERS spectra did depend on the thickness of the PMDI films. When the PMDI films were relatively thick (about 85 angstroms), the SERS spectra were similar to the normal Raman spectra of PMDI but when the PMDI films were relatively thin (about 15 angstroms), the spectra resembled those obtained from PMDI adsorbed onto silver island films. These results indicate that PMDI films are actually bilayers in which the molecules adjacent to the substrate have a preferred (end-on) orientation but those farther from the substrate have random orientation.

## V. Acknowledgements

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Table I. Tentative band assignments for phthalimide.

| Frequency ($cm^{-1}$) | | | |
|---|---|---|---|
| Raman | SERS | IR | Tentative Assignment |
| | | 3199(w) | ν(NH) |
| 1770(s) | | 1775(m) | ν(C=O), in-phase |
| 1740(m) | | 1753(m) | ν(C=O), out-of-phase |
| 1620(m) | | | ν(8b) |
| | | 1604(w) | ν(8a) |
| | 1475(w) | 1468(w) | ν(19b) |
| 1385(w) | | 1388(m) | ν(CN), imide II |
| 1320(s) | | 1308(m) | n(7a) |
| 1175(w) | 1175(m) | 1183(w) | ν(9a) |
| 1150(m) | 1155(m) | 1140(w) | ν(18a) |
| | | 1090(w) | ν(13) |
| | | 1053(m) | ν(CNC), imide III |
| 1020(m) | 1020(m) | | ν(18b) |
| 750(m) | | 746(w) | ν(1) |
| | | 716(m) | imide IV |
| 690(w) | 690(s) | | δ(CNC) |
| 650(w) | | 647(w) | δ(CNC) |
| 560(m) | | 550(w) | ν(6a) |
| | | 534(m) | ν(6b) |

S-strong, M-medium, W-weak

Table II. Tentative band assignments for pyromellitic diimide.

| Frequency ($cm^{-1}$) | | | | |
|---|---|---|---|---|
| Raman | SERS | IR | RAIR | Tentative Assignment |
| | | 3200(M) | 3204(M) | NH stretch |
| 1775(S) | | 1772(S) | 1779(S) | $\nu$(C=O), in-phase |
| 1748(W) | | 1720(S) | 1729(M) | $\nu$(C=O), out-of-phase |
| 1633(W) | 1624(W) | | | $\nu$(8a), ring stretch |
| | | 1567(W) | | $\nu$(19b), ring stretch |
| | | 1470(W) | 1471(W) | $\nu$(19a), ring stretch |
| 1368(M) | 1372(S) | 1379(M) | 1383(M) | CNC axial stretch |
| | | 1307(M) | 1311(S) | $\nu$(14), ring stretch |
| 1200(M) | 1202(M) | | | $\nu$(7a), CX stretch |
| | | 1156(M) | 1156(W) | $\nu$(13), CX stretch |
| | | 1062(M) | 1062(W) | CNC transverse stretch |
| | | 775(W) | 766(W) | $\nu$(20b), CX stretch |
| 762(M) | | | | $\nu$(1), ring stretching |
| | | 728(M) | 729(W) | CNC out-of-plane bend |
| | 690(S) | | | $\delta$(CNC) |
| 659(M) | | | | $\delta$(CNC) |
| | | 637(W) | 638(W) | $\nu$(12), ring stretch |
| 578(W) | 575(W) | | | $\nu$(3), CX in-plane bend |
| | | 560(W) | 563(W) | $\nu$(16a), out-of-plane bend |
| 520(W) | 517(W) | | | $\nu$(6b), ring stretch |

S-strong, M-medium, W-weak

Table III. Tentative band assignments for N-phenyl phthalimide.

| | Frequency | | | assignment |
|---|---|---|---|---|
| IR | NR | SERS | RAIR | |
| 1779(W) | 1785(M) | 1792(S) | 1780(W) | $\nu$(C=O) in-phase }imide I |
| 1735(M) | 1770(W) | 1778(M) | 1730(W) } | $\nu$(C=O) o.p.b. |
| 1708(S) | | | 1701(M) | |
| 1614(W) | 1622(W) | | | $\nu$(8b)-$C_6H_4$ |
| 1595(W) | 1611(M) | 1612(S) | | $\nu$(8a)-$C_6H_5$ |
| 1495(M) | 1508(W) | | 1502(M) | $\nu$(19a)-$C_6H_5$ |
| 1465(W) | 1475(W) | | | $\nu$(19b)-$C_6H_4$ |
| 1422(W) | 1435(W) | | | $\nu$(19b)-$C_6H_5$ |
| 1385(S) | 1395(S) | 1392(M) | 1386(M) | $\nu$(C-N-C), imide II |
| 1220(W) | 1233(W) | 1230(W) | 1220(W) | $\nu$(13)-$C_6H_5$ |
| 1174(W) | 1182(W) | 1180(W) | | $\nu$(9a)-$C_6H_5$ |
| 1157(W) | 1167(W) | 1172(W) | | $\nu$(9a)-$C_6H_4$ |
| 1117(M) | 1121(M) | 1125(S) | 1113(W) | $\nu$(C-N-C), imide III |
| 1080(W) | | | | $\nu$(18b)-$C_6H_5$ |
| 1067(W) | | | | $\nu$(13)-$C_6H_4$ |
| | 1039(W) | | | ? |
| 1024(W) | 1024(M) | 1025(S) | | $\nu$(18b)-$C_6H_4$ |
| 1002(W) | 1011(S) | 1015(S) | | $\nu$(18a)-$C_6H_5$ |
| 962(W) | 971(W) | | | $\nu$(5)-$C_6H_5$ |
| 916(W) | 925(W) | | | $\nu$(17a)-$C_6H_5$ |
| 881(W) | 893(W) | | | $\nu$(17b)-$C_6H_5$ |

| | | | | |
|---|---|---|---|---|
| 848(W) | 850(W) | | | $\nu$(10a)-$C_6H_5$ |
| 796(W) | 807(W) | | | $\nu$(12)-$C_6H_4$ or<br>C=O i.p.b. |
| 762(M) | | | 756(W) | $\nu$(11)-$C_6H_5$ |
| 720(M) | | | 716(W) | C-N-C o.p.b.<br>imide IV |
| 705(M) | 718(S) | 720(S) | 705(W) | $\nu$(1)-$C_6H_4$ |
| 690(W) | | | | $\nu$(4)-$C_6H_5$ |
| | 681(W) | 682(W) | | ? |
| | 643(W) | 640(W) | | imide ring i.p.b. |
| 627(W) | 628(W) | 625(W) | 627(W) | $\nu$(6b)-$C_6H_5$ |
| | 585(W) | | | $\nu$(6a)-$C_6H_4$ |
| 531(W) | | | | $\nu$(16b)-$C_6H_5$ |
| | 474(W) | 480(W) | | $\nu$(6b)-$C_6H_4$ |
| | 420(W) | | | $\nu$(6a)-$C_6H_5$ |

Table IV. Tentative band assignments for N, N-diphenyl pyromellitic diimide.

| | Frequency | | | |
|---|---|---|---|---|
| IR | NR | SERS | RAIR | Assignment |
| | 1801(S) | 1807(S) | | $\nu$(C=O), imide I |
| 1786(W) | | | 1785(W) | |
| 1724(VS) | | | 1722(W) | |
| 1701(VS) | | | | |
| | 1620(W) | | | $\nu(8a)-C_6H_2$ |
| 1599(W) | 1609(M) | 1614(M) | 1600(W) | $\nu(8a)-C_6H_5$ |
| 1503(M) | 1515(W) | | 1504(M) | $\nu(19a)-C_6H_5$ |
| 1453(W) | | | | $\nu(19b)-C_6H_2$ |
| | 1420(VS) | 1425(M) | | $\nu$(C-N-C), axial { imide II |
| 1399(S) | | | 1401(S) | |
| 1290(W) | | | | $\nu(3)-C_6H_5$ |
| | 1281(W) | 1286(W) | | $\nu(13)-C_6H_5$ |
| 1193(W) | | | 1194(W) | ? |
| | 1188(W) | | | $\nu(9a)-C_6H_5$ |
| | 1168(W) | | | $\nu(9a)-C_6H_2$ |
| 1130(S) | 1136(M) | 1140(W) | 1129(W) | $\nu$(C-N-C), transverse, imide III |
| 1071(W) | | | | $\nu(13)-C_6H_2$ |
| 1024(W) | 1035(W) | 1035(W) | | $\nu(18a)-C_6H_2$ |
| | 1008(S) | 1015(S) | | $\nu(18a)-C_6H_5$ |
| 918(W) | | | | $\nu(17a)-C_6H_5$ |
| 868(W) | | | 869(W) | $\nu(17b)-C_6H_5$ |
| 843(M) | 850(W) | | | $\nu(10a)-C_6H_5$ |

| | | | | |
|---|---|---|---|---|
| | 812(W) | | | $\nu$(12)-$C_6H_2$ or C=O i.p.b. |
| 742(S) | | | 742(W) | $\nu$(11)-$C_6H_5$ |
| | 740(VS) | 743(S) | | $\nu$(1)-$C_6H_2$ |
| 721(S) | | | | C-N-C o.p.b<br>imide IV |
| 687(M) | | | 686(W) | $\nu$(4)-$C_6H_5$ |
| | 643(M) | 645(M) | | imide ring i.p.b |
| | 625(W) | | | $\nu$(6b)-$C_6H_5$ |
| | 583(W) | 585(W) | | ? |
| | 570(W) | 575(W) | | $\nu$(6a)-$C_6H_4$ |
| | 430(W) | | | $\nu$(6a)-$C_6H_5$ |

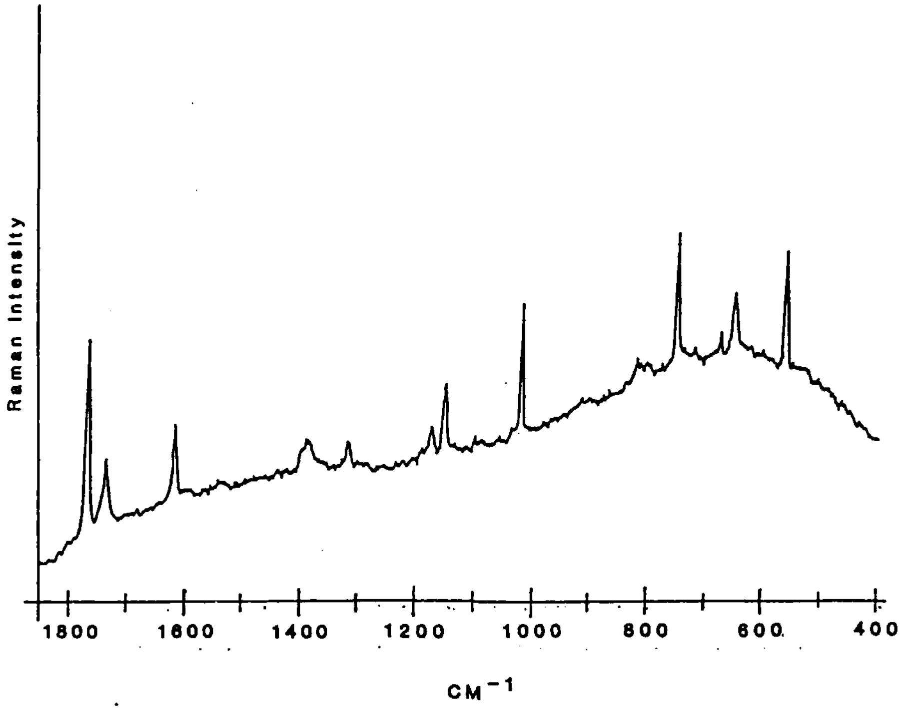


Figure 1. Normal Raman spectrum of phthalimide (PIMH).

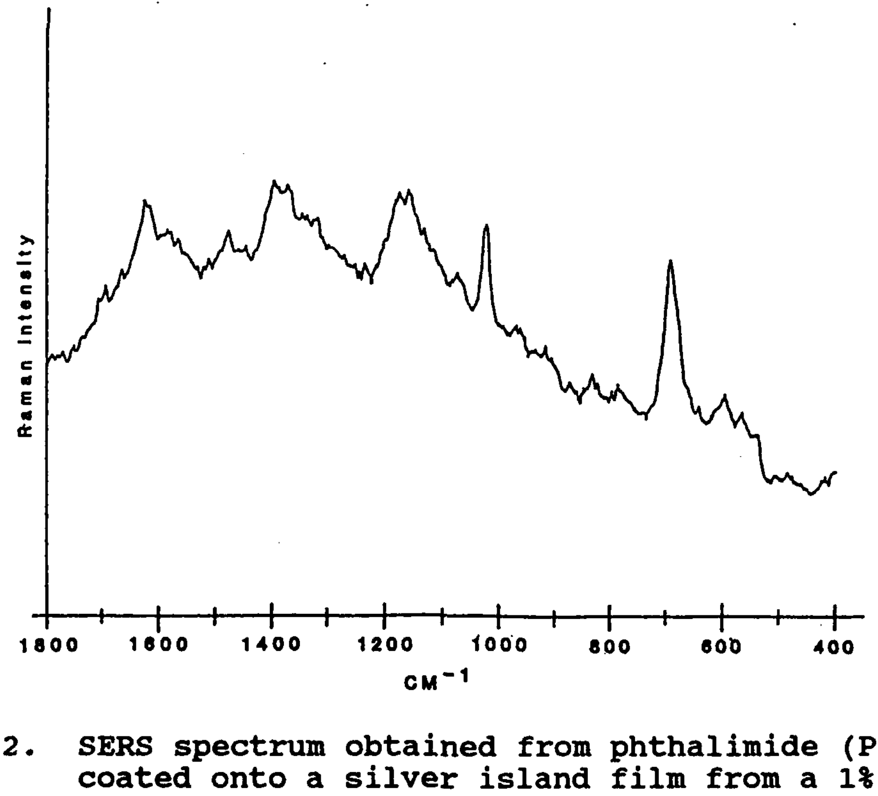


Figure 2. SERS spectrum obtained from phthalimide (PIMH) spin-coated onto a silver island film from a 1% solution in dimethylformamide.

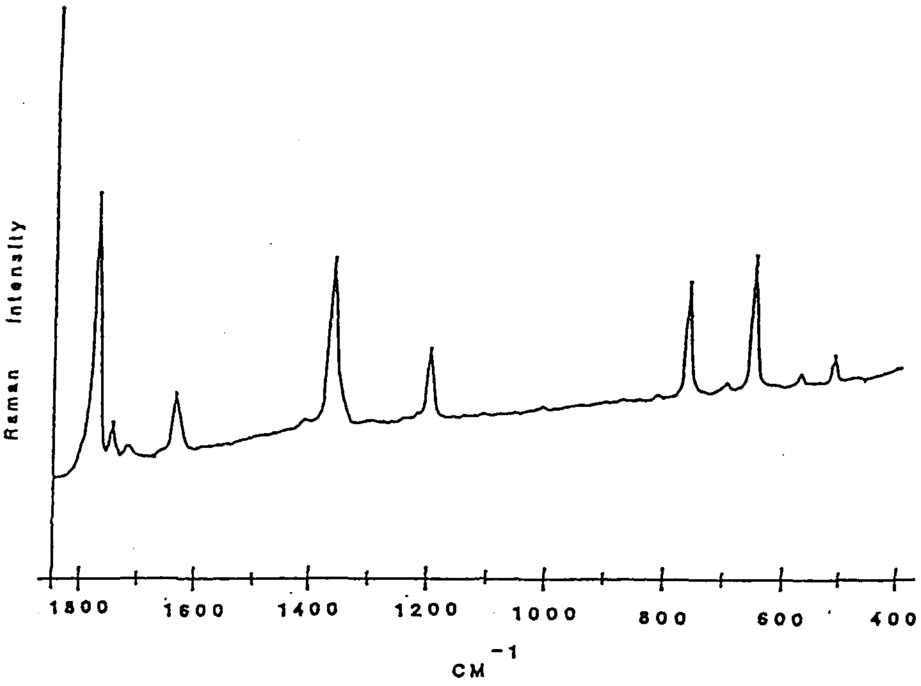


Figure 3. Normal Raman spectrum of pyromellitic diimide (PMDI).

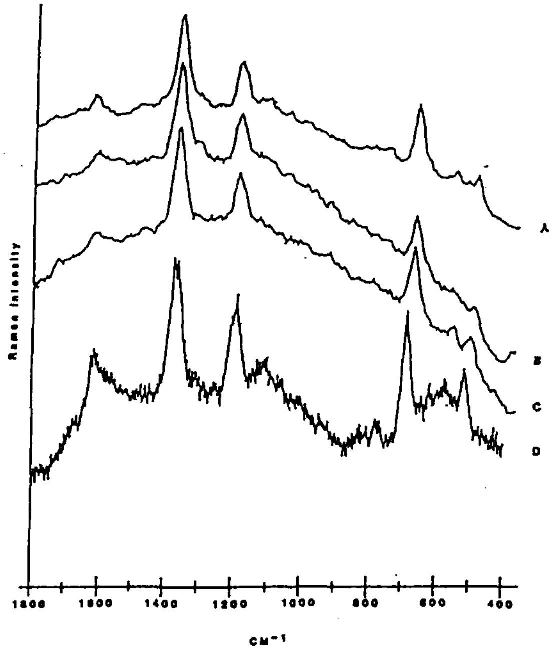


Figure 4. Surface-enhanced Raman spectra obtained from thin films of PMDI spin-coated onto silver island films from (A)-1%, (B)-0.1%, (C)-0.05%, and (D)-0.001% solutions.

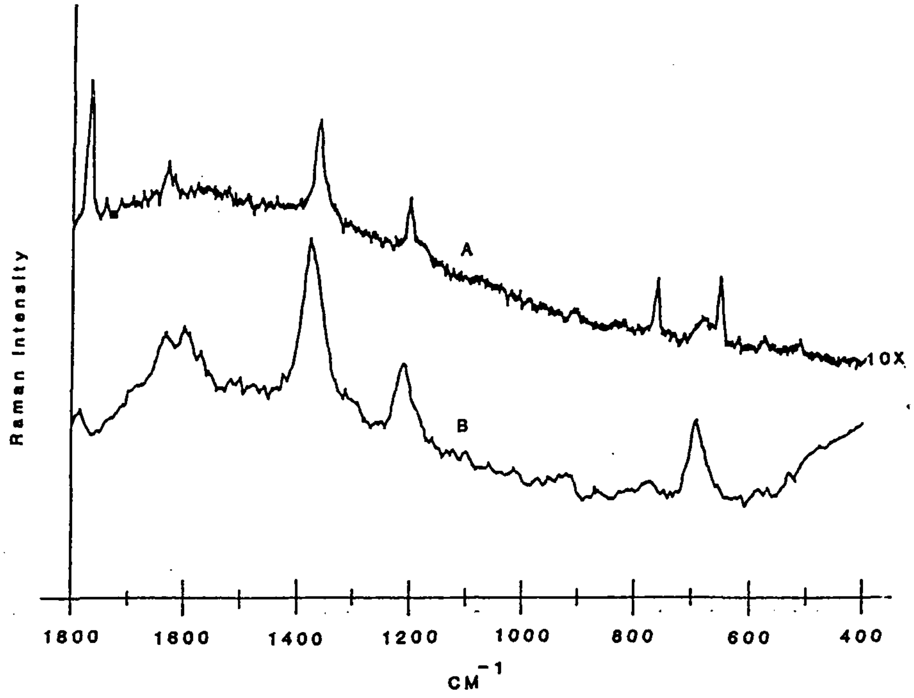


Figure 5. SERS spectra obtained from PMDI films deposited onto highly oriented pyrolytic graphite (HOPG) from (A)-2% and (B)-0.01% solutions and then overcoated with silver island films.

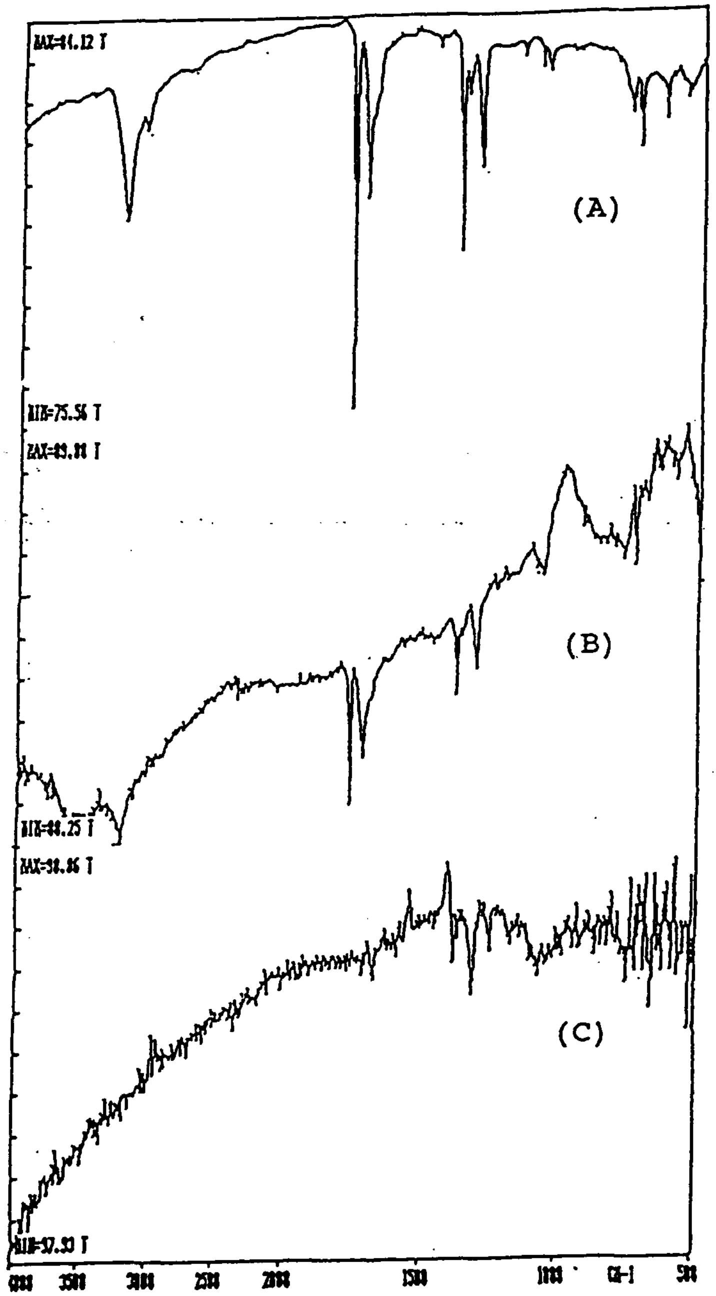


Figure 6. Reflection-absorption infrared spectra obtained from PMDI films spin-coated onto thick silver films from (A)-1%, (B)-0.1%, and (C)-0.01% solutions in dimethylformamide.

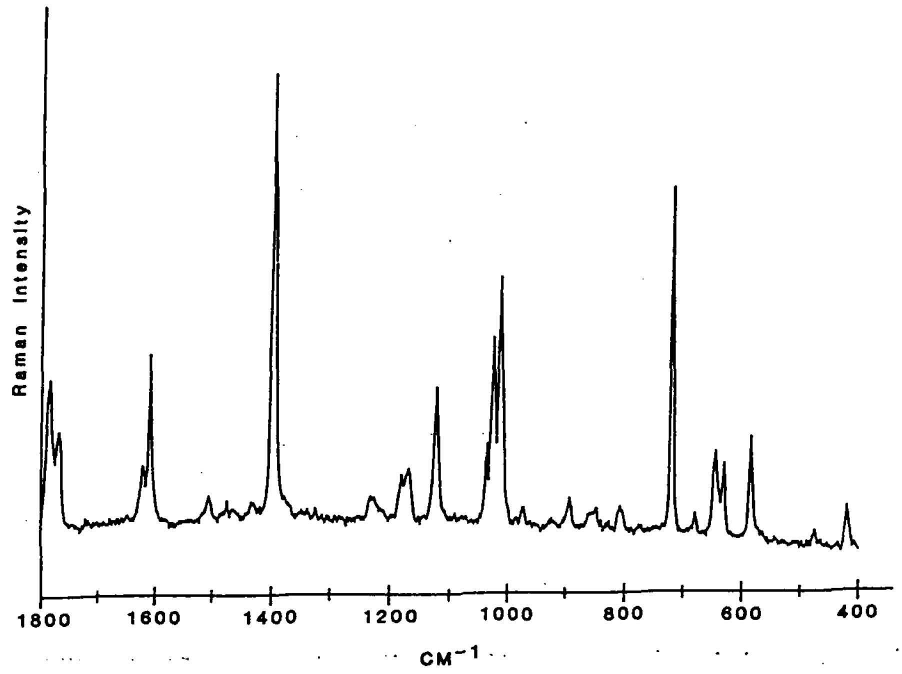


Figure 7. Normal Raman spectrum of N-phenyl phthalimide.

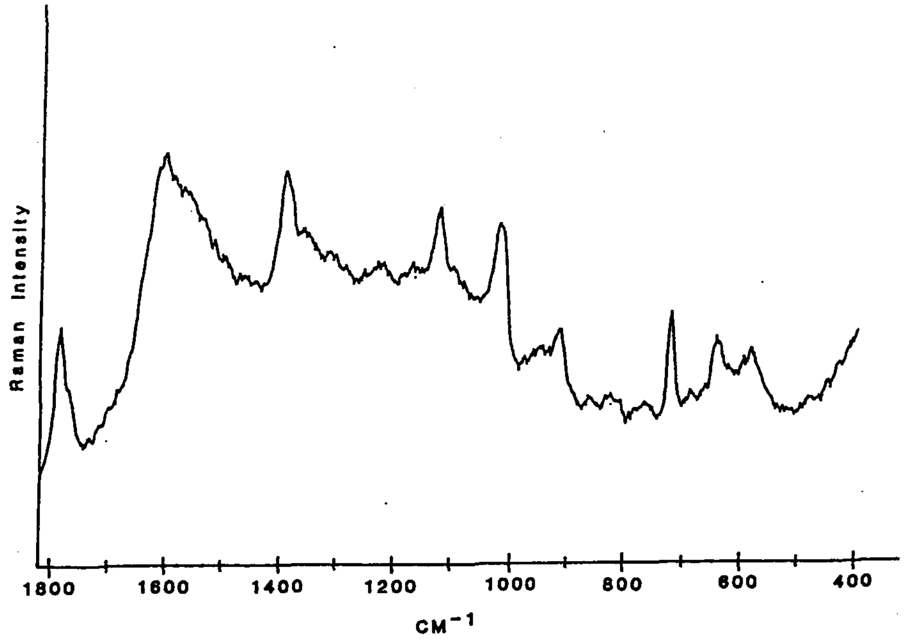


Figure 8. SERS spectrum of N-phenyl phthalimide spin-coated onto a silver island film from a 1% solution in dimethylformamide.

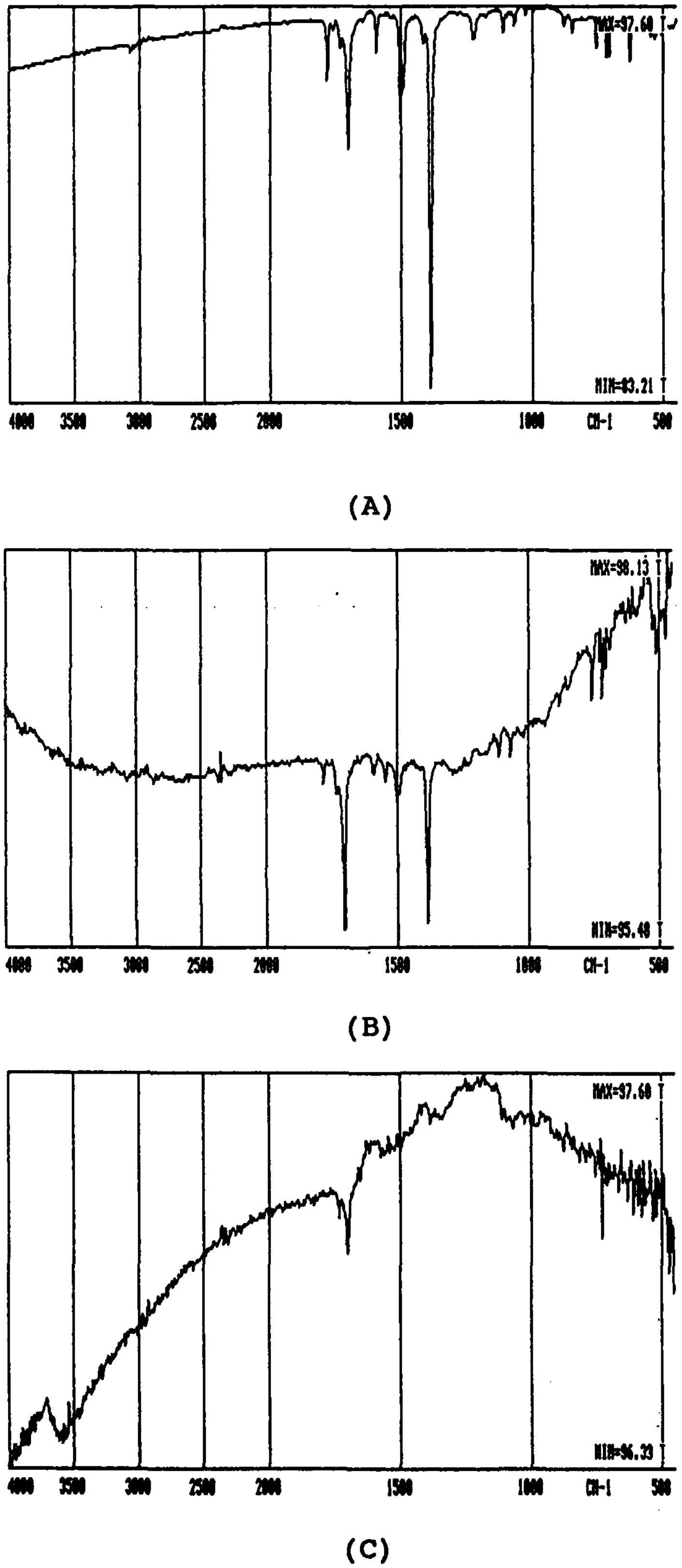


Figure 9. RAIR spectra obtained from N-phenyl phthalimide spin-coated onto thick silver films from (A)-1.0, (B)-0.1, and (C)-0.01% solutions in DMF.

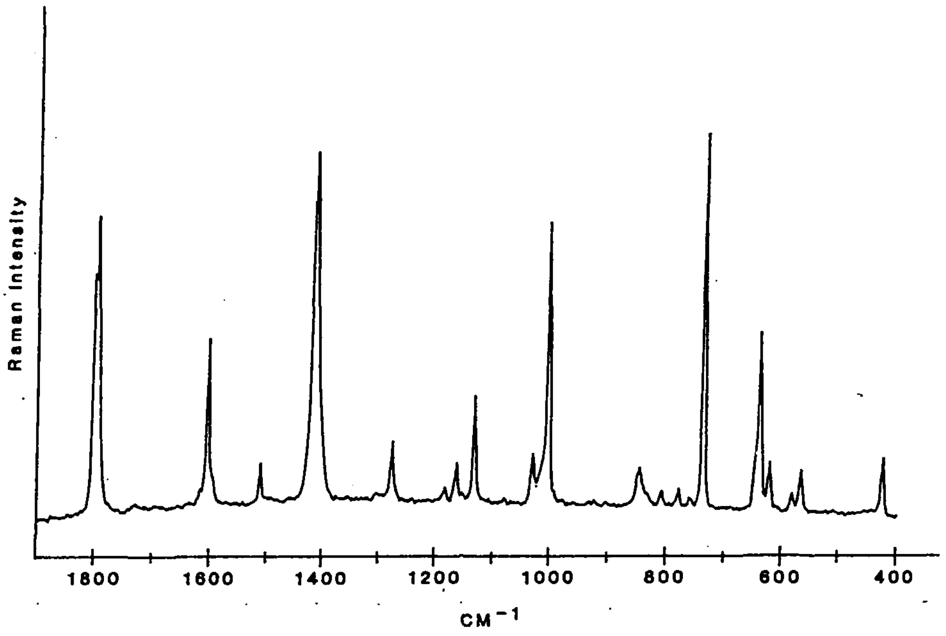


Figure 10. Normal Raman spectrum obtained from N, N-diphenyl pyromellitic diimide.

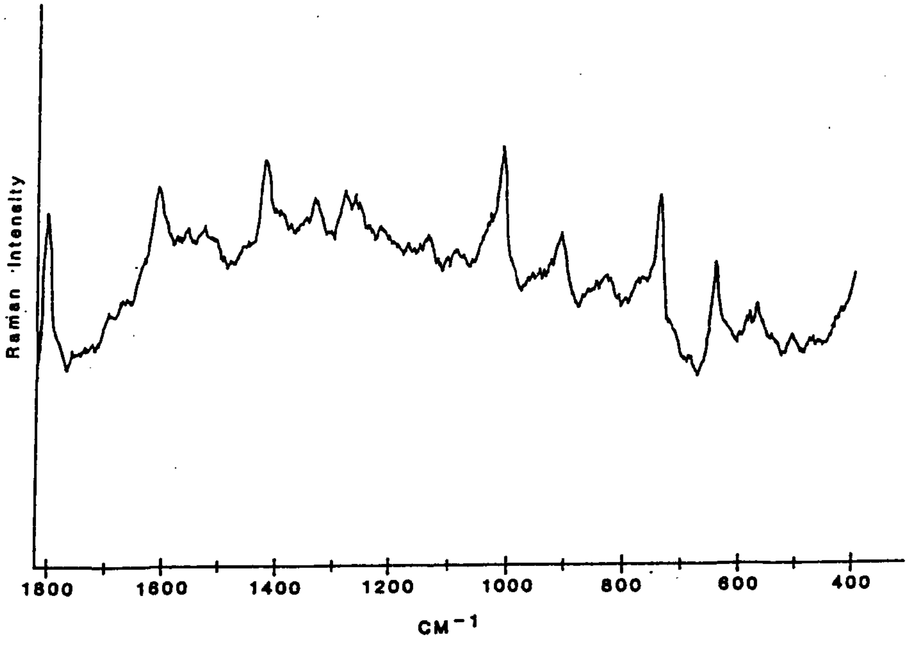
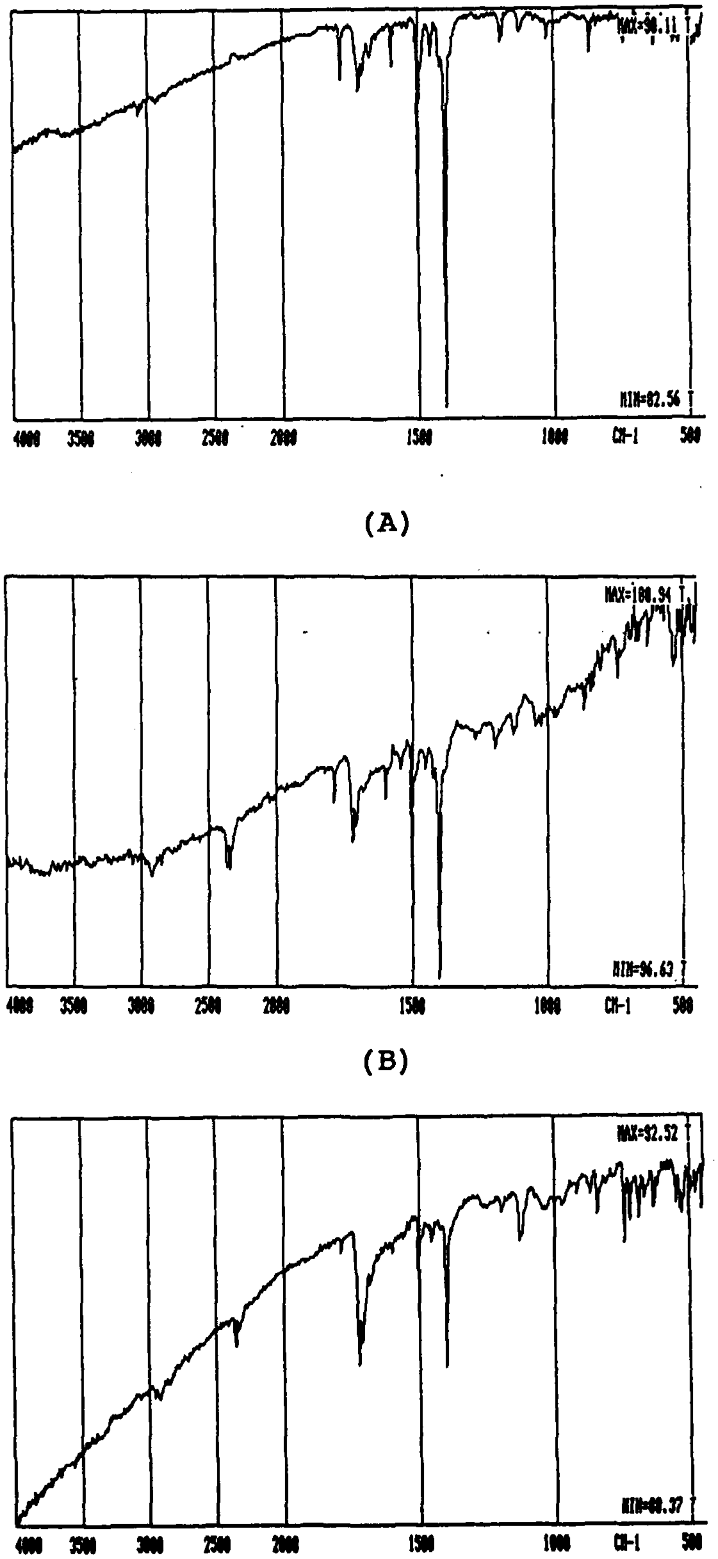


Figure 11. SERS spectra of N, N-diphenyl pyromellitic diimide deposited onto a silver island film from a 0.05% solution in hot DMF.



(A)

(B)

(C)

Figure 12. RAIR spectra of N, N-diphenyl PMDI films deposited onto thick silver films from (A)-0.05%, (B)-0.005%, and (C)-0.001% solutions in hot DMF.

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