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Surface enhanced spectroscopy of perylene derivatives.

Urmi. Guhathakurta

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SURFACE ENHANCED SPECTROSCOPY
OF PERYLENE DERIVATIVES

by

Urmı Guhathakurta

A Thesis
submitted to the
Faculty of Graduate Studies and Research
through the department of
Chemistry and Biochemistry in Partial
Fulfilment of the requirements for the
Degree of Master of Science at
the University of Windsor

Windsor, Ontario, Canada
1990
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ABSTRACT

SURFACE ENHANCED SPECTROSCOPY OF PERYLENE DERIVATIVES

by

Urmil Guhathakurta

Surface enhanced Raman (SERS), surface enhanced Resonance Raman (SERRS) of mono and multilayer films of three \( N,N' \)-unsymmetrical dialkyl-3,4:9,10-perylenebisdicarboximides, namely \( N \)-octyl-3,4:9,10-perylene tetra carboxylic mono anhydride (Oc-PTCDO), \( N \)-octyl-3,4:9,10-perylene tetra carboxylic mono imide (Oc-PTCDNH) and \( N \)-octyl,\( N' \)-isobutyl-3,4:9,10-perylene-bis(dicarboximide) (PBDC) have been studied and vibrational analyses have been attempted. SERS and SERRS of evaporated thin films of perylene, 3,4:9,10 perylene tetracarboxylic dianhydride (PTCDA) and 3,4:9,10 perylene tetracarboxylic \( N,N' \) bis (methyl) diimide (PTCDIME) on tin sphere, Ag island and Au island films are used to characterize the vibrations of the three unsymmetrical perylene derivatives. In resonance Raman (RRS) and SERRS the dominant bands are those of perylene chromophores as expected. There was no spectral evidence for a strong interaction of the molecule and the SERS active surface, and it was concluded that the LB layers were physisorbed onto the SERS active surfaces.

All three samples form aggregates due to intermolecular interactions within a single Langmuir Blodgett (LB) layer.
Electronic absorption of solution and solid films and surface enhanced fluorescence of LB layers on SERS active substrates were used to study aggregation reactions. It was observed that fluorescence signal of aggregate (excimer) is stronger in a neat layer whereas in a mixed layer (perylene derivative : arachidic acid) monomer emission is the dominant one.

It has been shown that SERRS is a unique technique to perform selective analytical spectroscopy of a specific layer in a bilayer sample. Monolayer assemblies of (t-bu)$_4$ VOPc and Oc-PTCDNH were used for the study.
DEDICATION

To Sarba
ACKNOWLEDGEMENTS

I take this opportunity to sincerely thank my supervisor, Prof. R. Aroca, for his meticulous supervision and untiring inspiration throughout the work. I would also like to thank all my friends, the technicians, the secretaries and the entire faculty of the Chemistry department at the University of Windsor.

Plus

A special word of thanks to the one and only – Doriano The Great.
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LIST OF ABBREVIATIONS

LB  Langmuir Blodgett
PTCDA  3,4,9,10 perylene tetracarboxylic dianhydride
PTCDIMe  3,4,9,10 perylene tetracarboxylic N,N’(di-methyl) diimide
Oc-PTCDO  N-octyl-3,4:9,10-perylene tetracarboxylic monoanhydride
Oc-PTCDNH  N-octyl-3,4:9,10-perylene tetracarboxylic monoimide
PBDC  N-octyl, N’-isobutyl-3,4:9,10-perylene-bis (dicarboximide)
RS  Raman Spectrum
RRS  Resonance Raman Spectrum
SERS  Surface Enhanced Raman Spectrum
SERRS  Surface Enhanced Resonance Raman Spectrum
UV-Vis  Ultraviolet Visible
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INTRODUCTION

(i) Applications:

Perylene tetracarboxylic derivatives have several applications in industry. They can be used as organic conductors or photoconductors\textsuperscript{1-8} in xerography and as dyes and pigments for colouring plastics\textsuperscript{9-12}. These organic compounds have excellent resistance to light, heat and solvents.

It was shown\textsuperscript{13} that the perylene diimides are highly photoconducting in the visible spectral range and therefore highly efficient in xerography using visible light. In another example\textsuperscript{5} conducting patterns have been generated in thin films of perylene tetracarboxylic dianhydride (PTCDA) using $3.2 \times 10^{-13}$ J Ar$^+$ irradiation. Resistivity was reduced by 14 orders of magnitude compared with that obtained for a non irradiated film with a concomitant change of color of film from red (as deposited) to dense, shiny black for highly conducting irradiated films. PTCDA and some of the substituted dimides are used industrially to dye plastics\textsuperscript{14}, polyesters and textiles\textsuperscript{15}.

Perylene tetracarboxylic derivatives can also be used as sensitizers for organic and inorganic photoconductors\textsuperscript{16}.
Perylene tetracarboxylic diimide (PTCDI) had been used in constructing photovoltaic elements which are used in producing an organic photoelectric solar cell\textsuperscript{17}.

(ii) Properties:
Chemical structural formulas of three perylene derivatives studied are shown in Fig. 1.
Nagao et al\textsuperscript{18} have synthesized a series of N,N’-unsymmetrical dialkyl-3,4;9,10 dicarboxiimides in which the alkyl groups are methyl, ethyl, propyl, butyl, isobutyl, pentyl, hexyl and octyl. They have evaluated the tinting strength and thermal decomposition of these compounds. Earlier the same group reported the synthesis of Oc-PTCDO and also the kinetic study of the reaction by spectroscopic techniques\textsuperscript{19}. No detailed spectroscopic study of these compounds have so far been made. In the present work, the absorption (UV-Vis and Infrared), emission and Raman scattering data for Oc-PTCDO ,Oc-PTCDNH and PBDC are reported.
For the first time we have obtained and tested the formation of Langmuir-Blodgett (LB) monolayers of these compounds. The spectroscopic characterization of LB layers was carried out using surface enhanced spectroscopy.
Figure 1. Chemical structural formula for N-octyl-3,4:9,10-perylenetetracarboxylic monoanhydride (Oc-PTCDO), N-octyl-3,4:9,10-perylenetetracarboxylic monomide (Oc-PTCDNH) and N-octyl,N'-isobutyl-3,4:9,10-perylene- bis(dicarboximide) (PBDC).
Figure 1
CHAPTER I
SURFACE ENHANCED RAMAN SPECTROSCOPY

Surface enhanced Raman spectroscopy (SERS) was first observed in 1974 by Fleischmann et al\(^{20}\) in an electrochemical experiment. An unusual increase of Raman intensity of pyridine adsorbed on a specially prepared silver electrode surface was observed and explained to be due to the increase of electrode surface area. A few years later Van Duyne et al\(^{21}\) and independently Creighton et al\(^{22}\) recognized that the large intensity could not be accounted for by the increase in surface area alone. Since then the effect has been observed from many molecules on different surfaces such as Ag, Au, Cu, Li, Na, K, Al, In etc. A complete list [up to 1986] of which can be found in a report by Seki\(^{23}\). Other than SERS, surface enhanced fluorescence, absorption, second harmonic generation and four wave mixing have also been observed\(^{24}\). Different types of surfaces have been used, the most common being the roughened electrode surface. In this case the surface is pretreated in one or more electrochemical oxidation-reduction cycles. Metal ions liberated in the oxidation half cycle are redeposited in reduction sweep as clusters of metal over the electrode surface, thus creating a roughness. Metal colloids prepared by reducing a dissolved metal salt by means of an appropriate reducing agent in either an aqueous or non aqueous medium\(^{25}\) are also SERS active surfaces. The third type of surface is island films consisting of small metal particles formed by vacuum evaporation and subsequent
deposition on a warm substrate. Metal vapour deposited on a cold substrate, namely cold deposited films are also suitable for SERS. In addition continuous films of the SERS active metals evaporated onto diffraction grating\textsuperscript{26} or onto rough CaF\textsubscript{2} substrate\textsuperscript{27} also shows SERS activity. In all these cases the essential requirement for a surface to be SERS active is that the surface has to have some roughness. Surface roughness helps to produce large local electromagnetic fields. According to the electromagnetic theory which is so far the most predictive theory of SERS, the largest contribution of enhancement comes from this local field enhancement due to the illumination of metal particles with electromagnetic field resonant or near resonant with the localized surface plasmon frequency of the metal structure. For metal spheroids with dimensions much smaller than the incident wavelength, the electric field inside is\textsuperscript{28}

\[ E_{\text{ins}} = \frac{E_0}{1 + \left(\varepsilon(w)/\varepsilon_0 - 1\right) A} \]

where \( E_0 \) is the incident laser field, \( \varepsilon(w) \) and \( \varepsilon_0 \) are the complex dielectric constants of metal particle and surrounding medium respectively and \( A \) is the depolarization factor whose value is completely determined by the shape of the particle\textsuperscript{29}. Incident field \( E_0 \) is in resonance with the surface plasmon mode whenever
\[
1 + \frac{\mathcal{E}(\omega)}{\mathcal{E}_0} - 1 \alpha = 0
\]

For a sphere \( \alpha = 0.333 \). Therefore for a large enhancement by the sphere the \( \text{Re}(\varepsilon) \) of the metal must be equal to \(-2\) (relative to the medium) at the excitation wavelength and also \( \text{Im}(\varepsilon) \) should be small at that wavelength. Copper, Ag, Au and the alkali metals satisfy these conditions very well, that is why these metals are favourable for SERS whereas the heavy transition metals which have \( \text{Re}(\varepsilon) = -2 \) only in far UV and have large values of \( \text{Im}(\varepsilon) \) at these wavelengths are unsuitable for SERS\(^{30}\).

In some cases an additional non-electromagnetic enhancement has been observed, where the molecule forms a strong chemical bond (chemisorption) to the surface. The extreme case occurs when a new electronic state, resonant with the exciting laser is created. The Raman scattering cross section increases by many orders of magnitude due to this resonance. Changes in Raman scattering cross section forms the basis for chemical enhancement theory. In contrast to the spectra of physisorbed molecules, in this case additional bands due to metal-molecule complex can be observed. Some of the vibrational bands are often shifted in frequency from those in bulk.

Other SERS mechanism, in addition to these two, have also been proposed but there is not much experimental support for these.

A few experimental observations in SERS are:
1. The spectra are depolarized. The variation of electric field of dipole and the distribution of molecular orientations over the surface give rise to large depolarization ratios.
2. For a physisorbed molecule the enhancement is of long range. Enhancement has been observed for molecules separated by tens of nanometres from the surface. Chemisorption, on the other hand, is of short range and usually the enhancement is maximum for the first monolayer in which molecule is in direct contact with the surface and decreases rapidly with the increase of number of layers.

3. Selection rules of SERS are totally different from those for bulk. Appearance of modes in SERS which are normally Raman inactive are not unusual.

4. SERS active surfaces usually give a broadband luminescence background.

5. The excitation profile deviates markedly from w^4.

SERS have been successfully applied in many areas of chemistry, such as chemical analysis, corrosion, lubrication and heterogeneous catalysis.

In addition to SERS other surface enhanced experiments like surface enhanced fluorescence, surface enhanced absorption, surface enhanced hyper-Raman scattering etc. are also flourishing.
LANGMUIR BLODGETT FILMS

Although formation of monolayers of oil films on water surface was studied by Benjamin Franklin in 1774, the theory of monolayers was developed only in 1930’s by Langmuir and Blodgett\textsuperscript{31-34}. In recent years there has been a rapidly growing interest in LB films with a wide range of technological applications including molecular electronics, microelectronics, integrated optics, and microlithography.

There are two characteristics of LB films of great importance, one is their single molecule nature, thickness of the order of nanometres can be made and the second one is the orientation of the molecules in monolayers.

The first direct practical application of insoluble monolayers on a large scale was the reduction of stored liquids due to evaporation by spreading monolayers over the liquid surface. It has been found that the straight chain compounds which form condensed monolayers at ordinary temperatures are the best evaporation retardants.

LB films have been successfully used in photovoltaic cells as insulators on a host of semiconductor surfaces, such as, Si, GaP, InP, CdTe and HgCdTe. The use of phthalocyanine based LB films in field effect semiconductor devices such as gas sensors has drawn particular attention.

Monolayer techniques can be used to estimate very small amounts of compounds, Hughes and Rideal\textsuperscript{35} actually used the technique to
provide a calibration for a sensitive microbalance.

Stepped multilayers have been made available commercially as thickness gauges. Blodgett used multilayers as antireflective coating on glass.

These are only a few of the numerous applications of LB films.

The essential components of the instrument for depositing LB films consist of a trough filled with a liquid subphase, usually water between two barriers one fixed and the other movable and a dipping device. A dilute solution (~ $10^{-4}$ M) of the substance to be studied is spread on the subphase. The volatile solvent evaporates and a monomolecular thick film is formed on the surface. The movable barrier is then compressed with a very slow speed and the corresponding surface pressure against area occupied by the monolayer on the trough is recorded. These plots are called "pressure - area isotherms".

For deposition of monolayers on a substrate the barrier is fixed at a constant pressure (determined from the isotherm) and the substrate is dipped in or out of the monolayer covered water. On a hydrophilic substrate such as glass the film will not be deposited on the first downstroke, the first monolayer is formed on the upstroke. There are three types of dipping, X, if the substrate is immersed only, in Y deposition the substrate is dipped followed by withdrawal and in Z type the film is formed by withdrawal only.

Our objective was to study SERS and SERRS of LB films of PTCDO, PTCDNH and PBDC on Ag island and tin sphere films.
CHAPTER II

EXPERIMENTAL

(a) Vacuum Evaporation System

SERS active thin metal films were prepared in a Balzers instrument. A typical pressure before evaporation was 133.3x10^{-6} Pa. The thickness was monitored with an Inficon XTM quartz crystal oscillator. Corning 7059 glass slides were used as substrates. Three different types of films were prepared:

i) Ag island films were prepared by the evaporation of 5 or 10 nm of silver at the rate of .1 nm/sec on the Corning glass slide held at 473 °K. Transmission electron micrographs of a 10 nm Ag film is shown in Fig 2.

ii) Au island films were prepared by the evaporation of 4 nm of gold on a slide held at 473 °K. Fig 3 shows the transmission electron micrograph of a 4 nm thick Au film.

iii) Ag coated Sn spheres were formed by evaporating 100 nm mass thickness of Sn at a rate of .5 nm/sec onto glass substrate held at 393 °K. 100 nm of Ag was then overlaid at the same rate with the substrate held at room temperature. The silver layer was deposited after vacuum cleaning the system for at least one
Figure 2. Transmission electron microscopy of a 10 nm Ag island film.
Figure 3. Transmission electron microscopy of a 4 nm Au island film.
Figure 4. Transmission electron microscopy of a Ag coated Sn sphere.
hour. Fig 4 shows the transmission electron micrographs of a tin sphere.

Thin films of perylene, PTCDA and PTCDIME of thicknesses between 2 nm & 6 nm were prepared on SERS active surfaces in a different vacuum deposition system used for organics only. Separate boats were used for all of them. The same Inficon XTM quartz crystal oscillator was used to measure the thickness. The rate of evaporation varied from .1 nm/sec to .5 nm/sec.

(b) Spectroscopic System

(i) Raman

Four laser lines, 488.5 nm (blue) and 514.5 nm (green) from Spectra Physics model 164 Ar+ and 568.2 nm (yellow) and 647.1 nm (red) from Spectra Physics model 2020 Kr+ laser were used to detect Raman spectra. Raman shifts were measured with a Spex 1403 and a Ramanor U-1000 double monochromator with microscopic attachment for backscattering geometry. An IBM PC microcomputer was used to drive the stepper motor connected to the two 1800 grooves/nm holographic gratings. The microcomputer also acquired the signals from a thermoelectrically cooled Hamamatsu R955 multialkali photomultiplier tube followed by conventional photon counting. Two separate software programs were used, one for data acquisition, another for data manipulation. Typical spectral bandpass and
laser power were 5 cm$^{-1}$ and 100 mw respectively. Polarization. Polarization measurements were made using a polarization rotator (Spectra Physics model 310-21) which is mounted on 164 Ar$^+$ and 2020 Kr$^+$ lasers. The scattered light was resolved into parallel and perpendicular (to the incident plane) components using a linear polarizer. To compensate for the instrument polarization, a polarization scrambler was placed between slit and the analyzer. Four polarized spectra were routinely measured SS, SP, PS and PP. (The ratio SP/SS was 0.75 for the 314 cm$^{-1}$ line of CCl$_4$) where S means light polarized perpendicular to the plane of incidence (the plane containing incident & scattered light) and P means light polarized parallel to the plane of incidence. The first letter gives incident beam polarization and the other one the analyzer. In Porto’s notation$^{38}$ this is Z(YY)X=SS, Z(YZ)X=SP, Z(XY)=PS, Z(XZ)X=PP. For example, for a right angle scattering, the rotation Z(YY)X indicates incident light propagating in the Z direction and polarized in the Y direction which is scattered into the X direction with Y polarization. In the experimental geometry the ZX plane was the plane of incidence. Fig 5 shows a schematic of experimental arrangement used.

(ii) Infrared transmission and UV-VIS absorption spectra.

Infrared transmission spectra in KBr pellets were measured in a FTIR Nicolet 5DX instrument. Transmission was measured from 400-4000 cm$^{-1}$ with a resolution of about 4 cm$^{-1}$. 
Figure 5. Schematic of experimental arrangement used to record polarization spectra. Direction of propagation of laser beam was along Z axis and collection was along X axis.
Figure 5
UV-VIS absorption spectra were run on a HP 8451 diode array spectrophotometer.

(c) Langmuir Blodgett Film

LB mono and multilayer films on SERS active surfaces and on clean glass surfaces were prepared on a Lauda Langmuir film balance equipped with an electronically controlled dipping device Lauda Filmlift FL -1. A schematic diagram of the trough is given in Fig 6. The water used in the trough was Zenopure followed by another filtration by milli-Q. All isotherms and film transfers were done at room temperature. The subphase used was 2.5*10^{-4} M CdCl_{2} solution in water with a pH of about 5.7. The monolayers were deposited by withdrawal (Z deposition) and subsequent multilayers by immersion followed by withdrawal (Y deposition). The dipping/withdrawal rate was 4.8 mm/min for all films. To prevent the vibration the trough was placed on a stone plate and to prevent dust contamination the whole system was kept in a box. The trough was cleaned thoroughly before making each film.

(d) Chemicals

Purified Oc-PTCDO, Oc-PTCDNH and PBDC were provided by Prof. Y. Nagao. These were used as received without further purification. The solvents used were spectrograde toluene and chloroform (BDH).
Figure 6. A schematic of a Langmuir Blodgett trough.
PTCDA and PTCDIMe were synthesized and purified at the laboratories of Xerox research centre of Canada.
CHAPTER III

RESULTS AND DISCUSSION

(a) Perylene, PTCDA and PTCDIME

Vibrational Characterization

To characterize the vibrations of unsymmetrical perylene derivatives, SERS and SERRS of perylene, PTCDA and PTCDIME on different SERS active surfaces, such as Ag island film, Au island film and on tin sphere have been studied. Electronic absorptions of all three of the compounds were in resonance with the 488 nm laser line (blue) and in off resonance with the 647.1 nm (red) laser line.

Perylene. The reference for the assignment of molecular vibrations in PTCDA and PTCDIME is the parent perylene molecule. For comparison, SERS spectra of perylene evaporated onto Ag and Au films were obtained. Excitation with the 488- and 514.5-nm lines of a 6-nm film of perylene on a 10-nm Ag island film produced spectra similar to those reported by Baranov\textsuperscript{38} on colloidal Ag. Three intense bands were observed at 1292, 1368, and 1571 cm\textsuperscript{-1}, and in the low-frequency region two bands of medium relative intensity were detected at 352 and 550 cm\textsuperscript{-1}. All of these Raman bands have been previously assigned to totally symmetric \( a_g \) vibrations\textsuperscript{39}. SERS of a 6-nm perylene film on gold, obtained with the 647.1-nm laser line, was also dominated by the same totally symmetric vibrations: two strong bands at 550 and 1292 cm\textsuperscript{-1}, but the relative intensities of the 352-, 1368-, and 1571-cm\textsuperscript{-1} bands were lower than in the Ag
SERRS. It was concluded that a number of frequencies (other than those listed above) observed in 1200-1600 cm\(^{-1}\) region of the RRS spectrum of perylene may be due to non-totally-symmetric vibrations, probably of \(b_g\) type. Fig 7 shows the SERS and SERRS of perylene on Ag and Au island film.

PTCDA Similar to perylene the RRS spectra of thin solid films of PTCDA showed a number of "doublets" reminiscent of solid state splitting\(^{40}\). The molecular vibrational spectra of a 2-nm film of PTCDA on Ag and Au films, obtained with the 488-nm line, are shown in Fig. 8. The SERRS spectra from both surfaces are identical, although the enhancement factor was larger for Ag than Au. The SERRS spectra obtained at submonolayer coverage clearly indicated that all bands in RRS spectra of solid films should be assigned to the isolated molecule. All frequencies are listed in Table I. Experiments with Ag-coated Sn spheres made it possible to obtain SERS and SERRS on the same substrate as shown in Fig. 9. However, the RS excited with the 647.1-nm line (SERS) of PTCDA on Ag showed some significant differences. The centre of the C-H bending vibration was seen at 1292 cm\(^{-1}\) (1304 cm\(^{-1}\) in SERRS), the ring stretching vibration was observed as a broad band at 1374 cm\(^{-1}\), and in the low region a new band at 274 cm\(^{-1}\) was observed, while the relative intensity of the C-O-C bending vibration was negligible. When the thickness of the evaporated film is increased 25nm\(^{41}\), the bandwidth decreases, the 1374 cm\(^{-1}\) band recovers its strong relative intensity, but the 274 cm\(^{-1}\) band is no longer observed with the 647.1-nm line. The spectral evidence suggests that PTCDA molecules directly attached to the metal surface are chemisorbed, forming a
Figure 7. SERRS of a 6 nm film of perylene on 10 nm Ag [(a) and (b)] and SERS of 6 nm film of perylene on 4 nm Au film (c).
Figure 7
Figure 8. SERRS of a 2 nm film of PTCDA on Ag (top) and on Au (bottom) island films.
Figure 9. SERS (top) and SERRS (bottom) of 4 nm film of PTCDA on Ag coated Sn sphere.
## TABLE I

Observed Raman Frequencies (cm\(^{-1}\)) of PTCDA

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<td>274 m</td>
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<td>233 m</td>
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weakly bonded metal complex, probably through the oxygen atoms. As a result of chemisorption, a bandwidth broadening was observed, and new bands were seen in the spectrum. Increasing the PTCDA coverage results in lower absolute intensities, bandwidth narrowing, and changes in relative intensities. Lower absolute intensities could be explained in term of plasmon damping\textsuperscript{42} by the layers of molecular dye, since the measured absorbance of the Ag film decreased when overcoated with PTCDA. Bandwidth narrowing and changes in relative intensities should be due to large surface-enhanced scattering contributions from physisorbed PTCDA molecules. For thick dye films the RS was very weak on a strong fluorescence background. The previous interpretation of results was supported by the fact that SERS of PTCDA, obtained at low coverage, on a 4-nm Au film was characterized by narrow bandwidths and frequencies at 1304, 1381, 1572, and 1591 cm\textsuperscript{-1}, indicating that there was no chemisorption of PTCDA on Au.

PTCDIME Similar to PTCDA, the RRS spectrum of 200nm PTCDIME film contained a number of "doublets" (1290 and 1301, 1570 and 1587 cm\textsuperscript{-1}, and low-frequency shoulder for the band at 1381 cm\textsuperscript{-1}). SERRS of PTCDIME, obtained at submonolayer coverage on the rough surface (2-nm thickness for Ag and Au island films, and a 4-nm film for the Sn/Ag substrate), were identical in frequencies and relative intensities for all three substrates as illustrated by the top spectra on Figs.10 and 11. Since all the RRS frequencies were seen in SERRS, they should be assigned to molecular species, excluding the possibility of interpreting some of the Raman bands as due to
solid-state effects in the submicrometer PTCDIME films. For the Ag-coated Sn spheres SERS with large signal to noise ratio were obtained for both excitation lines 488 nm (in resonance with the molecular electronic transition) and 647.1 nm (SERS) as shown in Figure 10. The corresponding frequencies are listed in Table II. By comparison with the RRS plot, it can be seen that the SERS spectrum contains one strong C-H bending band at 1291 cm\(^{-1}\) (the second C-H bend at 1301 cm\(^{-1}\) is the strongest signal in SERRS). Similarly, the non-totally-symmetric stretching vibrations of the benzene ring have negligible relative intensity under 647.1-nm excitation. It seems reasonable to assume that the intensity pattern observed in RRS and SERRS is due to intensity borrowing by the Herzberg-Teller mechanism in RRS, and therefore the 1301-, 1370-, and 1587-cm\(^{-1}\) bands could be assigned to \(b_{1g}\) symmetry type.

SERS of PTCDIME on Au film is shown on Figure 11 (bottom spectrum). The spectra were obtained with 2nm of PTCDIME evaporated onto 4nm of Au, which amount to a surface coverage of less than a monolayer, in this particular case a large number of vibrational frequencies were registered and the spectra were polarized. Notably, many vibrational bands with considerable relative intensity were present in the low-frequency region. With the help of SERS selection rules\(^{43,44}\), the observation may be rationalized in terms of a predominant molecular orientation on the surface. Therefore, for PTCDIME molecule face-on on the Au surface (principal \(C_2\) perpendicular to the surface), strong enhancement should be expected for the \(a_{2g}\), \(b_{2g}\), and \(b_{3g}\) symmetry species, in
Figure 10. SERS (bottom) and SERRS (top) of 4 nm film PTCDIMe on Ag coated Sn spheres.
PTCDIME S-spectra

SERRS LL=488nm

SERS on Sn/Ag spheres LL=647.1nm

WAVENUMBERS

Figure 10
Figure 11. SERS (bottom) of 2 nm film of PTCDIMe on Au and SERRS (top) of 2 nm film of PTCDIMe on Ag island film.
PTCDIMA
SERRS on Ag. LL=488nm

SERS on Au   LL=847.1nm

Wavenumbers

Figure 11
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correspondence with the fact that the normal component of the local field is much stronger than the tangential component. Since the last two types are out-of-plane vibrations, which are normally observed with frequencies below 900 cm\(^{-1}\), it is thus possible to explain the presence of a large number of low-frequency vibrations. Polarization measurements also seem to support a preferred face-on molecular orientation, since S- and P-polarized light produce different patterns of relative intensities. However, when the thickness of the PTCDIME film was increased to 6nm the spectrum recovered the intensity pattern of SERS on silver. The specific orientation of physisorbed molecules at low coverage is lost with increasing surface coverage, and the SERS spectra become depolarized (identical S and P spectra).

Polarization
The polarization properties of RAMAN bands observed in SERS and SERRS for molecules physisorbed or chemisorbed onto metal surfaces are clearly different from depolarization ratios measured in gas or liquid samples\(^{43}\). It is normally found that totally symmetric and non-totally-symmetric vibrations are observed with a constant depolarization ratio (similar ratio of SP/SS intensities). This ratio is higher than the known values for totally symmetric modes, and it is said that SERS and SERRS spectra are depolarized. In this sense all SERRS spectra measured here were depolarized. SERS measurements were also depolarized with the exception of the low coverage SERS of PTCDIME on gold. Another interesting point was the efficiency of S- and P-polarized light to produce surface
enhancement. Under similar conditions an S spectrum (incident light S polarized, with the electric vector parallel to the substrate surface) and a P spectrum were recorded for each sample. For all substrates and laser excitation of 488 nm, the absolute intensity of the S spectrum was consistently higher than that of the P spectrum. Therefore, for SERRS $I_S > I_P$. It should be pointed out that for the same geometry in the RRS of 200-nm films $I_P > I_S$. For SERS on all three substrates (excitation with the 647.1-nm laser line), the reverse was observed, i.e., $I_P > I_S$. It could be speculated that the P-excited surface plasmons were more efficiently damped by the molecular dye than S-excited plasmons in this set of SERRS experiments.

**Surface Coverage**

The coverage dependence in SERRS was studied experimentally (for the CoPc molecule) and theoretically by Zeman et al.\textsuperscript{42} In this work the conclusion was that the negative dependence of SERRS with increase in coverage was due to the quenching of the surface plasmon resonance by the adsorbate. The experimental results of the present work indicate that the coverage dependence of SERRS is negative with the maximum occurring well below a monolayer coverage. Coverage dependence studies of SERS were hindered by a very large increase in the fluorescence signal with film thickness. Since the PTCDA and PTCDIME dyes strongly absorb in the visible region, the present results obtained with the 488-nm laser line seem to support the physical explanation that negative dependence of SERRS intensities with coverage is due to strong damping of the
metal particle resonance by the dye.

(b) Oc-PTCDO, Oc-PTCDNH and PBDC

**Infrared**

The Infrared transmission spectra of Oc-PTCDO, Oc-PTCDNH and PBDC in KBr pellet are shown in Figs 12,13 and 14 respectively. Since these molecules have no symmetry, all vibrational modes are allowed, and a large number of frequencies were observed. However, it was possible to assign some of the characteristic frequencies of the perylene tetracarboxylic chromophore and those of the aliphatic chain. In Oc-PTCDO four distinct C=O stretching frequencies were observed. Two of them at 1696 cm⁻¹ and 1656 cm⁻¹ corresponding to the stretching modes of the C=O of the imide group as observed in PTCDI and two carbonyl stretches of the anhydride group at 1766 cm⁻¹ and 1723 cm⁻¹ in agreement with the corresponding frequencies of PTCDA. In the two imide compounds Oc-PTCDNH and PBDC, all carbonyl stretching vibrations were observed below 1700 cm⁻¹, in agreement with the characteristic carbonyl frequency of the imide group or alkyl substituted imide group. Characteristic C=C stretching vibrations of the perylene ring were observed in all three molecules around 1579 & 1595 cm⁻¹. Out-of-plane C-H modes of the perylene ring were also prominent in the IR spectra at 810 cm⁻¹ and 743 cm⁻¹ for Oc-PTCDNH, 810 cm⁻¹ and 739 cm⁻¹ in Oc-PTCDO and 809 cm⁻¹ and 746 cm⁻¹ in PBDC. A large number of aliphatic and aromatic C-H bending frequencies were observed in 1000-1500 cm⁻¹. Three strong IR bands around 2853,2927 and 2952 cm⁻¹ corresponding to the C-H
Figure 12. Infrared transmission spectra of Oc-PTCDO in KBr pellet.
Figure 13. Infrared transmission spectra of Oc-PTCDNH in KBr pellet.
**Figure 14.** Infrared transmission spectra of PBDC in KBr pellet.
stretching vibrations of the octyl group were seen in all three compounds. Observed frequencies are listed in Table III.

**UV-Vis absorption** Electronic absorption spectra of Oc-PTCDO, Oc-PTCDNH & PBDC in solution are shown in Fig 15. The solvents were toluene for Oc-PTCDNH and PBDC & chloroform for Oc-PTCDO. It is clear from the figures that all three samples are in resonance with 488 and 514.5 nm laser lines but in off resonance with 647.1 nm line.

**Raman Spectra** Resonance Raman spectra of Oc-PTCDO & Oc-PTCDNH films on glass and PBDC in KBr pellet are shown in Figs. 16, 17 and 18 respectively. For all three sample RRS were very simple and entirely due to vibrational fundamentals of the chromophore group, i.e., there were no observed vibrational fundamentals of the octyl radical. Three intense bands, similar to what was observed for perylene, PTCDA, PTCDI-Me were also seen for Oc-PTCDO and Oc-PTCDNH at 1298, 1379 and 1572 cm\(^{-1}\). The 1298 cm\(^{-1}\) band corresponds to a C-H locally symmetric bending vibration, whereas the higher frequencies have been given the general assignment of perylene ring stretching vibration.

**Surface Enhanced Resonance Raman Spectra** SERRS were very simple and almost same as RRS. In the low frequency region of the RRS one band of medium relative intensity was detected at 541 cm\(^{-1}\), while in SERRS a second band was observed at 557 cm\(^{-1}\) for Oc-PTCDNH, and 555 cm\(^{-1}\) for Oc-PTCDO and PBDC. These vibrational frequencies are
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Figure 15. UV-Vis absorption spectra of (a) Oc-PTCDO in chloroform, (b) Oc-PTCDNH in toluene and (c) PBDC in toluene.
Figure 16. RRS of 0c-PTCDO film on glass obtained with 514.5 nm laser line. This spectrum was recorded using a backscattering arrangement.
Figure 16

Graph showing wavenumbers (cm\(^{-1}\)) against counts/sec. Peaks at 737, 558, 380, and 201 counts/sec with wavenumbers ranging from 100.0 to 1800.0 cm\(^{-1}\). Structure of a molecule with labels R65, L65.5, and film on glass.
Figure 17. RRS of Oc-PTCDNH film on glass obtained with 514.5 nm laser line. Polarization was P<sub>r</sub>.
Figure 18. RRS of PBDC in KBr pellet obtained with 514.5 nm laser line. This spectrum was recorded using a backscattering arrangement.
clearly due to perylene ring deformation. Observed Raman shifts are listed in table IV. There was no spectral evidence for a strong interaction of the molecule and the SERRS active surface, and it was concluded that the LB layers were physisorbed onto the SERS active surfaces. SERRS of Oc-PTCDO on Ag island and Sn/Ag film are shown in Figs. 19 and 20 respectively. SERRS of Oc-PTCDNH on same two substrates are shown in Figs. 21 and 22. Fig. 23 shows the SERRS of PBDC on Sn/Ag film. Fig. 24 is the SERS spectrum of Oc-PTCDO on Sn/Ag film.

Aggregation in LB films.

Molecular aggregation of polyaromatic molecules in the solid state is one of the major factors that determine physical and photophysical properties of solid structures. Molecular organization has been studied, for example, in evaporated and also in LB films of pyrene using fluorescence technique, in LB films of molecular dyes. Perylene is also known to form dimers in the solid state, and the fluorescence spectra of solid perylene, can be explained only in terms of excimer emission. We have studied the aggregation of LB films of PTCDO, PTCDNH and PBDC by uv-vis absorption and fluorescence of solution and solid films and enhanced fluorescence on SERS active substrates.

Absorption : All three samples, OC-PTCDO, OC-PTCDNH and PBDC, in solution present characteristic absorptions of polycyclic aromatics in the visible region of the electromagnetic spectrum, as can be
### TABLE IV

Observed SERRS Frequencies (cm$^{-1}$) of Oc-PTCDO, Oc-PTCDNH and PBDC

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<td>1450 w</td>
<td>1454 w</td>
<td>Ring stretch</td>
</tr>
<tr>
<td>1572 vs</td>
<td>1572 vs</td>
<td>1572 vs</td>
<td>Ring stretch</td>
</tr>
</tbody>
</table>
Figure 19. SERRS of 1 LB of Oc-PTCDO on Ag island film excited with 514.5 nm laser line. Polarization = $S_\pi$. 
Figure 20. SERRS of 1 LB of Oc-PTCDO on Sn/Ag film excited with 514.5 laser line. Polarization= P⊥.
**Figure 21.** SERRS of 1 LB of Oc-PTCDNH on Ag island film

excited with 514.5 nm laser line. Polarization=$P_r$. 
Figure 22. SERRS of 1 LB of Oc-PTCDNH on Sn/Ag film excited with 514.5 nm laser line. Polarization=SS.
Figure 23. SERRS of 1 LB of PBDC on Sn/Ag film excited with 514.5 nm laser line. Polarization = P₀.
Figure 23

SEERS on Sn/Ag
IL=514.5nm

CH3(CH2)7-N

CH3(CH2)7-CH2-CH3

5225 3956 2687 1418

Wavenumbers (cm⁻¹)

Counts/sec
Figure 24. SERS of 1 LB of Oc-PTCDO on Sn/Ag film excited with 568.2 nm laser line. Polarization=S\textsubscript{r}. 

seen in Figs 25, 26 and 27 respectively. Oc-PTCDO and PBDC had two
strong absorption bands at 487 and 522 nm and 490 and 526 nm
respectively which are due to the monomeric form of the dye. The
Oc-PTCDNH however showed in addition to two bands at 487 and 526
another band at 580 nm. This particular band becomes the most
prominent feature in the absorption spectrum of thin solid film of
PTCDNH (Fig. 26), an indication of the formation of aggregates, the
absorption spectra of thin solid films of PTCDO (Fig. 25) and PBDC
(Fig. 27) also showed new bands at 564 and 576 nm respectively
which were not present in solution spectra and therefore could be
assigned to molecular aggregates. Therefore, from the above results
it can be concluded that OC-PTCDNH form aggregates both in solution
and in thin solid films, whereas Oc-PTCDO and PBDC form aggregates
only in thin solid films.

Fluorescence: Figs. 28 and 29 show the fluorescence spectra of
dilute solution of Oc-PTCDNH and PBDC in toluene (top spectra in
both) and fluorescence spectra of a thin solid film of Oc-PTCDNH
and PBDC on glass (bottom) respectively. It can be seen that in both
the cases the solution spectra has three bands, the most intense
band being that at 530 nm for Oc-PTCDNH and at 536 for PBDC. The
fluorescence spectra of thin solid films, on the other hand, has
only one strong band at 674 nm for Oc-PTCDNH and at 680 nm for
PBDC. It was concluded that since in solution the concentration of
monomer was much more than that of aggregates, the monomer band was
stronger in solution, whereas in solid film since monomer was
hardly present the fluorescence spectra of solid film were
Figure 25. Absorption spectra of Oc-PTCDO - $5 \times 10^{-5}$ M solution in chloroform (lower trace) and film on glass (upper trace).
Figure 26. Absorption spectra of Oc-PTCDNH - 5*10^{-5} M solution in toluene (lower trace) and film on glass (upper trace).
Figure 27. Absorption spectra of PBDC - $5 \times 10^{-5}$ M solution in toluene (lower trace) and film on glass (upper trace).
**Figure 27**

Absorbance of a film on glass with the chemical structure of 1,1'-binaphthyl-2,2'-diamine (NBD).
Figure 28. Fluorescence spectra of Oc-PTCDNH in solution (top) and of a solid film on glass (bottom).
Figure 29. Fluorescence spectra of PBDC in solution (top) and of a solid film on glass (bottom).
dominated by the fluorescence band due to aggregates.

Surface enhanced fluorescence. To study the fluorescence LB films of all three samples were made on Ag island and Sn/Ag substrates. The pressure area isotherm for Oc-PTCDO gave an area per molecule of .51 nm\(^2\) at surface pressures between \(10^{-2}\) and \(3.5\times10^{-2}\) N/m (Fig. 30). The transfer of monolayer was carried out at \(10^{-2}\) N/m. The pressure-area isotherm for Oc-PTCDNH gave an area per molecule of .18 nm\(^2\) (Fig. 31), indicating the formation of aggregates in the LB film. The isotherm of PBDC was broad with transitions of limiting areas of 1.05 and .55 nm\(^2\) (Fig. 32). The transfer of the monolayer was carried out at \(2\times10^{-2}\) N/m, a pressure that correspond to a compressed monolayer. Since the calculated area for the perylene tetracarboxylic diimide group is ca. .75 nm\(^2\) (hydrocarbon chains excluded), which was much more than the area per molecule obtained at the transfer pressure in all three cases it is possible that the PTCD group was tilted on the water surface for all three of them. In contrast to the fluorescence spectra of solutions, the fluorescence spectra of neat LB films of PTCDNH and PBDC show a strong emission band at 640 & 648 nm respectively, a similar broad emission was characteristic of excimer formation in perylene and perylene derivatives\(^{39}\). At the same time the emission from the monomers were not observed, a clear indication of extensive aggregation in the LB film. To elucidate the aggregation, the mixed monolayers of Oc-PTCDNH and arachidic acid and PBDC and arachidic acid were then prepared. In both the cases a molar ratio of 1:10 (dye : arachidic acid) was maintained. The spectra of 3 mixed
Figure 30. Surface pressure - area isotherm of a neat Oc-PTCDO LB layer.
Figure 31. Surface pressure -area isotherm of a neat Oc-PTCDNH LB layer.
SURFACE PRESSURE–AREA ISOTHERM
NEAT Oc–PTODNH ON WATER

Figure 31
Figure 32. Surface pressure - area isotherm of a neat PBDC LB layer.
Figure 32

Surface Pressure-Area Isotherm Neat PBDC on Water

Surface Pressure (mN/m) vs. Area/Molecule (nm²)
layers of PTCDNH on Sn/Ag and 3 mixed layers of PBDC on Ag island film are shown in Figs. 33 & 34. In both the cases the fluorescence signal of the monomer were clearly seen, together with the surface enhanced Raman, confirming the presence of isolated monomers in the mixed layers.

The enhanced Raman & fluorescence of 1, 3 & 7 mixed LB layers of PBDC on Sn/Ag are presented in Fig 35. For the first LB layer SERRS was seen without interference from fluorescence because fluorescence enhancement is competing with the metal quenching of fluorescence. Due to the long range nature of the electromagnetic enhancement and to the fact that metal quenching for the second and further layers decreases the fluorescence signal increases steadily as it can be seen in Fig 35.

SPATIAL TUNING
In this section it has been shown how SERRS can be used to perform selective vibrational characterization of a specific layer in a bilayer sample without apparent interference from adjacent material.
For monomolecular layers or mixed layers with submonolayer concentrations, molecular sensitive analytical techniques are needed to study, for instance, chemical reactions in LB monolayers and changes due to interactions at the interface. SERS and SERRS provide both molecular specificity and sensitivity for monolayer and submonolayer quantities. By tuning into the molecular resonances
Figure 33. SERRS of 1 LB layer of neat Oc-PTCDNH on Sn/Ag (upper trace), and surface enhanced fluorescence (lower trace) of 3 LB of mixed (1:10 mole ratio) Oc-PTCDNH : Arachidic acid monolayer.
Figure 33
Figure 34. Surface enhanced scattering and fluorescence of 3 neat and 3 mixed (1:10 mole ratio of PBDC:Arachidic acid) LB layers on 10 nm Ag island film.
Figure 34

- 3 MIXED LB LAYERS ON Ag

3 NEAT LB LAYERS ON Ag →

531 nm

648 nm

1000.0
2000.0
3000.0
4000.0
Figure 35. Scattering and fluorescence enhancement of mixed LB layers of PBDC on Ag coated Sn spheres excited with 514.5 nm laser line.
and plasmon resonances of the enhancing surfaces and using the fact that electromagnetic enhancement is of long range, the spectral properties of one specific layer in a bilayer sample was determined.

Two molecular dyes, Oc-PTCDNH and (t-butyl)$_4$ VOPc were used for the study. Two different monolayer assemblies were prepared (Fig. 37). The 647 nm Kr$^+$ laser line is in resonance with the red absorption band of (t-Bu)$_4$ VOPc, and the 514.5 nm line of the Ar$^+$ laser is in resonance with the main absorption maximum of the Oc-PTCDNH, while the 568.2 nm line is in the preresonance region of the Pc molecule. Therefore, excitation with the 647.1 nm line of, for instance, a mixture of both molecular dyes would give the spontaneous Raman spectrum of the Oc-PTCDNH and the resonant Raman spectrum of (t-Bu)$_4$ VOPc or SERS and SERRS in the case of surface-enhanced effect. The opposite holds for excitation with the 514.5 nm laser line. Since SERRS would give rise to a signal to noise ratio at least 2 orders of magnitude higher than SERS, a selective spectroscopic identification of the component in the mixture can be attained by tuning into the appropriate molecular resonance$^{49}$.

In Fig 38, the bottom spectrum was obtained for sample A, which consisted of a Oc-PTCDNH LB monolayer deposited onto Ag-coated Sn spheres (the SERS active surface), and covered with one LB monolayer of (t-Bu)$_4$ VOPc. Since the 514.5 nm exciting line was in resonance with the molecular absorption of Oc-PTCDNH, the fundamental vibrations of this molecule dominated the spectrum, and it should be labelled SERRS of Oc-PTCDNH. The upper traces in
Figure 36. Chemical structures of (tert-butyl)$_4$ vanadyl phthalocyanine [(t-Bu)$_4$ VOPc] and N-octyl-3,4:9,10-perylenetetracarboxylic monoimide (Oc-PTCDNH).
(t-butyl)$_4$VOPc

Oc-PTCDNH

**Figure 36**
**Figure 37.** Schematic of (t-butyl)$_4$ VOPc and Oc-PTCDNH LB layers on Sn/Ag film.
**Figure 37**

Diagram labeled B:

- PTCDNH
- VOPc
- Sn/Ag

Diagram labeled A:

- VOPc
- PTCDNH
- Sn/Ag
the same figure were obtained for the same sample A but under 647.1-nm excitation, showing that SERRS signals of the upper LB layer of (t-Bu)$_4$VOPc were stronger than the SERS signals from the Oc-PTCDNH layer directly attached to the metal surface. Since the upper layer was obviously detached from the Ag surface, the strong SERRS signal is due to electromagnetic enhancement, which has been shown to extend far out the surface$^{50}$. Clearly, the spectroscopic tuning was possible due to the fact that SERRS at a distance is stronger than the SERS of the monolayer directly attached to Ag surface.

The spectra of the second sample (sample B) are shown in Fig. 39. The lower trace was obtained with 647.1-nm laser line, given the SERRS of (t-Bu)$_4$VOPc monolayer directly physisorbed onto the Ag. By tuning into the molecular resonance of Oc-PTCDNH (514.5-nm) the vibrational spectrum of the second layer becomes dominant, indicating once again that the SERRS of Oc-PTCDNH at a distance was also stronger than the SERS from the (t-Bu)$_4$VOPc monolayer located in the immediate vicinity of the Ag surface. For laser lines that are not within the main absorption of one of the two molecular resonances, the spatial spectroscopic tuning would not be possible, and spectra with strong vibrational fundamental from both layers could be observed. For example, in Fig.40 the spectrum of sample A obtained with the 568.2-nm laser line is shown, where both the vibrational fundamentals of the bottom layer (Oc-PTCDNH) and the upper monolayer of (t-Bu)$_4$VOPc contribute to the Raman spectrum. The sample B with the reverse order of LB layers, under 568.2-nm
Figure 38. SERRS from sample A under two different excitation wavelengths.
Figure 39. SERRS from sample B under two different excitation wavelengths. Pc bands in SERRS spectrum of Oc-PTCDNH are shown with shaded area.
excitation, gave the spectrum of (t-Bu)$_4$ VOPc. This result was in agreement with the fact that 568.2-nm was in preresonance region of the Pc electronic transition, but it was outside of the absorption region of Oc-PTCDNH.

The spatial spectroscopic tuning may be used to study a variety of sequential monomolecular assemblies for instance, to follow the interaction and spectral changes in separate monolayers containing donor and acceptor species or a chemical binding (reaction) that could affect one specific layer. In general, SERRS could be used for selective spectroscopic analysis of an LB monolayer in a matrix of spacers of molecules transparent to the exciting electromagnetic field.
Figure 40. Surface enhanced Raman spectra from samples A and B obtained with 568.2 nm laser line.
Adjacent LB layers on Ag/Sn Spheres

LL = 568.2 nm

A 685

B (t-butyl)₄VOPc

Figure 40

INTENSITY
CONCLUSIONS

In the present work, the electronic and the vibrational spectroscopic data of three unsymmetrical perylene tetracarboxylic derivatives are reported.

For the first time, Langmuir-Blodgett monolayers of these compounds have been deposited on SERS active substrates. The spectroscopic characterization of these layers was then carried out using surface enhanced spectroscopy. There was no spectral evidence for strong interaction of the molecule and the SERS active substrates and it was concluded that the LB layers were physisorbed onto the substrates.

Molecular aggregation of LB films of these compounds has been studied by surface enhanced fluorescence. It was observed that the fluorescence signal of aggregate (excimer) is stronger in a neat layer whereas in a mixed layer (diluted with arachidic acid) monomer emission is the dominant one.

A new spectroscopic technique "Spatial Spectroscopic Tuning" has been demonstrated. Two molecular dyes (t-bu)$_4$ VOPc and Oc-PTCDNH have been used for the study. It has been observed that SERRS of a specific layer in a bilayer sample [1 LB of Oc-PTCDNH and 1 LB of (t-bu)$_4$ VOPc on SERS active substrates] can be observed without apparent interference from the second layer. This technique can be
used to study a variety of sequential monomolecular assemblies.
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VITA AUCTORIS

URMI GUHATHAKURTA

BIRTHDATE :  July 23, 1959     Calcutta, India

EDUCATION :  1976 - 1982     Calcutta University
             Calcutta, India

              1983 - 1988     Indian Association for
                      the Cultivation of
                      Science
                      Calcutta, India

              1988 - 1990     University of Windsor
                      Windsor, Canada