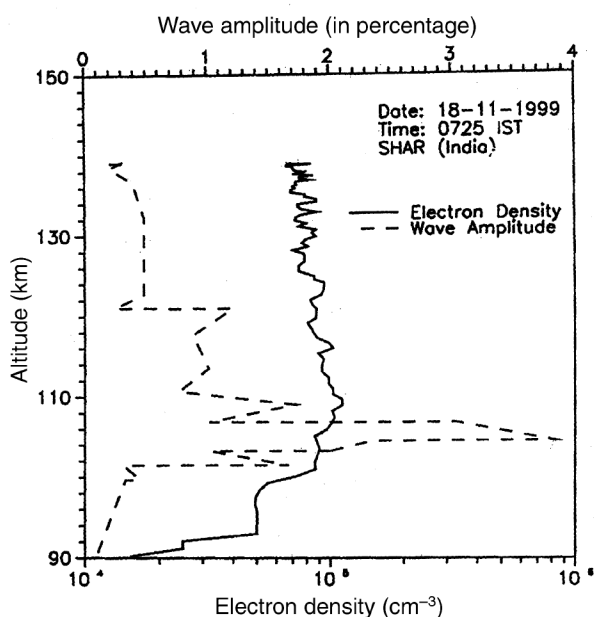


**Figure 1.** *a*, Telemetry record of plasma waves at around 105 km observed on 18 November 1999; *b*, Expanded portion of figure corresponding to the time interval of 99.02 to 99.04 s.



**Figure 2.** Altitude profiles of amplitude of plasma waves along with electron densities observed on 18 November 1999.

amplitude of plasma waves at 105 km where electron density gradient is negligibly small reveal that the causative mechanism for the generation of these plasma waves is different from well known gradient drift waves<sup>5-7</sup> observed over low latitudes. The fluctuations observed near the rocket apogee are non-geophysical in nature<sup>5</sup> and are associated with subsonic motion of the rocket<sup>10</sup>.

The plasma waves of a few meter scale sizes over magnetic equator are known to exist as type I waves<sup>8,11,12</sup> when the electron drift velocity driven by Hall polarization field associated with equatorial electrojet exceeds ion thermal velocity (350 m/s). As the polarization field associated with equatorial electrojet reduces by an order of magnitude over Sriharikota<sup>13</sup>, the type I waves are unlikely to exist over low latitude. Several rocket flight experiments<sup>7</sup> conducted earlier from Sriharikota and the radar experiments<sup>6</sup> from nearby site located 100 km west of this station also support the non-existence of type I wave over such location. Thus, an experimental evidence for a new kind of plasma wave over low latitude during Leonid 99 meteor storm is reported in this communication.

Once the gold sol was produced, it was stored in a glass vial. For each SERS measurement 0.5 ml of gold sol was taken in a quartz cuvette and to that was added the analyte (so that the final concentration ranges in the described range). After that  $\text{MgCl}_2$  (or  $\text{NaCl}$ ) solution in appropriate amount (so that the final concentration remained as 0.004 M) was added to the solution. The SERS measurements were done after 30 min.

All reagents were of analytical reagent (AR) grade and used without further purification. Gold chloride and TX-100 was purchased from Aldrich. All solutions were freshly prepared. 200 proof ethanol and double distilled water were used throughout.

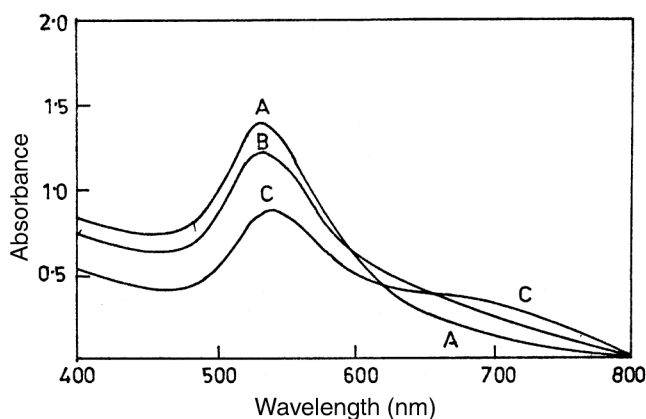
The photochemically prepared gold sol thus produced showed maximum absorbance at 523 nm. The reproducibility was excellent. During preparation irradiation up to 40 min did not produce any spectral change in the absorption spectra. TX-100, which acts both as a reducing agent and a stabilizer, appears to perform these two functions very efficiently. As a reducing agent it has the capability of reducing Au (III) to Au (0) in a mild way. At the same time it offers excellent stability to keep the sol in good condition.

The TEM studies showed the nanosized and non-spherical nature of the particles (Figure 1). The average size ranges from 30 to 70 nm. Although spherical nature for the gold is more common, the non-spherical nature might occur in surfactant media.

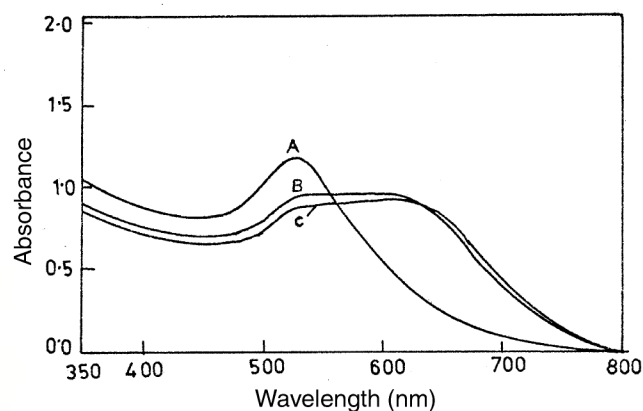
An important feature of the sol nanoparticles is its exceptional stability. The sol can be stored for more than three months and still remains good as a SERS substrate. No change in SERS spectrum is noticed for pyridine even when the sol is kept for several hours after the addition of pyridine. Since in this procedure TX-100 itself acts as a reducing agent and that too photochemically, the possibility of the presence of local excess of strong reducing agents often encountered in chemical reduction could be

avoided. Thus the photoreduction here is much more homogeneous in comparison to the chemical reduction procedure. As a consequence it is more probable here to obtain an ideal gold solution in a non-ionic micellar medium.

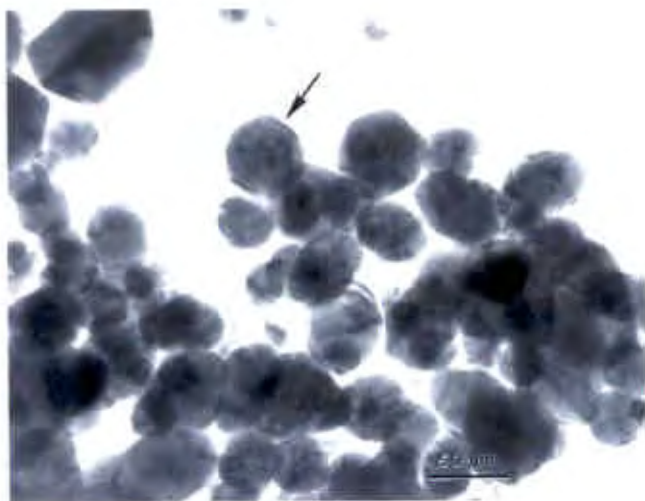
It is known that the absorption and the scattering properties of colloidal solutions of gold and silver are drastically affected by the changes of particle size, shape or aggregation. These changes can be induced by the addition of various chemicals to the colloidal solution<sup>21,22</sup>. Hence aqueous solutions of either  $\text{NaCl}$  or  $\text{MgCl}_2$  in the range of 0.02 to 0.004 M was added to the gold sol after its formation in order to induce special colloidal aggregation and its effect on the absorption spectra was studied. Figure 2 shows how in addition to the peak at  $\lambda_{\text{max}} = 523 \text{ nm}$  (curve A) due to the gold sol another peak appears due to the aggregation of the particles caused by the presence of 0.01 M  $\text{NaCl}$  (Figure 2, curve B) and 0.02 M  $\text{MgCl}_2$  (Figure 2, curve C). Also the presence of pyridine ( $10^{-5} \text{ M}$ ) causes the plasmon band due to gold (Figure 3, curve A) to be red-shifted (Figure 3, curves B and C) with time. Thus in addition to the absorption in the 523 nm region the sol has now absorption in the



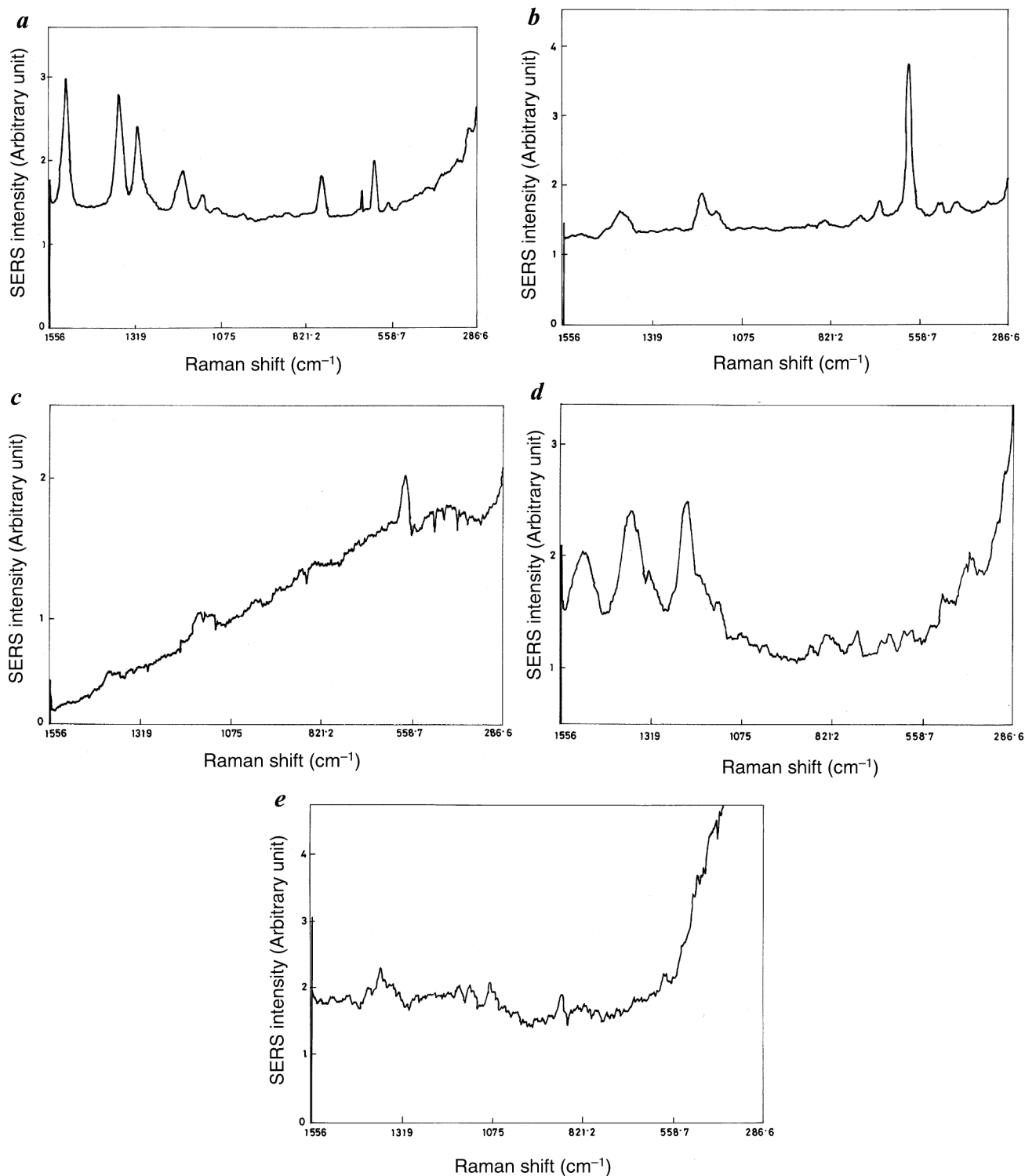
**Figure 2.** Effect of  $\text{NaCl}$  on gold sol. Curve A, Gold sol; Curve B, Gold sol with 0.01 M  $\text{NaCl}$ ; Curve C, Gold sol with 0.02 M  $\text{MgCl}_2$ .



**Figure 3.** Effect of addition of pyridine onto the gold sol. Curve A, Gold sol; Curve B, Gold sol with pyridine ( $10^{-5} \text{ M}$ ) at 10 min time interval; Curve C, Gold sol with pyridine ( $10^{-5} \text{ M}$ ) at 20 min time interval.



**Figure 1.** TEM of photochemically prepared gold sol.



**Figure 4.** SERS spectra of (a) Rhod 6 G; (b) CFV; (c) BCB; (d) 3-aminopyrene; (e) Gold sol blank.

630 nm region. The spectrum was recorded after 10 min of addition of pyridine. Longer time period to 1 h did not cause any further change in the absorption spectra. This type of spectral shift in the absorption maximum has previously been attributed to special type of colloidal aggregation, which is very important for SERS<sup>7,22</sup>. Due to this

type of change in the extinction spectra of the gold sol, the Kr laser excitation at 647.1 nm had better resonance of the optical fields with the surface plasmon.

Since surface enhancement of vibrations is dependent upon the orientation of the molecule on the surface and also since it is sensitive to the environment and structure

of the chromophore, SERS studies using gold nanosol with various types of compounds have been undertaken.

The study of the interaction of an adsorbed dye, in both its ground and excited states, with the energy states of the conduction band or surface plasmon of a metal is of much interest. This aspect of adsorbed dye is already discussed for dyes adsorbed on transparent metallic films as well as other supports. Little studies were done, however, on the phenomenon of dyes adsorbed on metallic colloids in aqueous solution. SERS can provide an insight into the interaction of dye molecules with metal surface. Moreover, many of the dyes are so sensitive towards SERS that even single molecule detection is possible<sup>23–25</sup>. Some dyes are also used as indicators or virus adsorptive to soil. Some are used as biomarkers as well as markers to trace and follow the extent to which the effluents in water streams travel and their concentration. Some of the dyes such as cresyl fast violet (CFV) were used as a label in the hybridization probes in the detection of DNA molecules<sup>26</sup>. Hence we felt it pertinent to test the feasibility of the gold sol for dye-SERS studies. We tested Rhodamine 6G (Rhod 6G), Cresyl fast violet (CFV), and Brilliant cresyl blue (BCB) with the gold sol prepared photochemically and obtained excellent results (Figure 4a–c). The concentrations are in the range of  $10^{-6}$ – $10^{-7}$  M. As we look into the structures of all three dyes, we see in all of them the presence of aromatic amino function. Eosin Y that contains no amino group but contains carboxylic acid function showed no SERS activity. All the dyes selected here are strongly SERS-active as tested earlier with different other substrates.

Detailed discussions on the analysis of the SERS spectrum of CFV were presented earlier<sup>25</sup>. In our case also the nature of the spectrum is similar. The most intense peak at  $589\text{ cm}^{-1}$  appearing in the SERS spectrum of CFV has a close resemblance to the peak that appeared in the SERS spectrum of BCB, which has similar functionalities as that of CFV. The appearance of several intense peaks in the SERS spectrum of Rhod 6G could be assigned to the vibrations as reported earlier<sup>24</sup>.

To test the potential of the photochemically prepared gold sol, we have selected several model compounds also, with various functionalities and having strong SERS activity. They are pyridine, 3-amino pyrene, nicotinic acid, nicotinamide, p-amino benzoic acid, and p-nitro benzoic acid. Although all of them are SERS-active substances with solid substrates, we detected strong SERS signal for 3-amino pyrene ( $10^{-4}$  M) (Figure 4d) only, and not with nicotinic acid, nicotinamide, p-amino benzoic acid, and p-nitro benzoic acid (all having concentration in  $10^{-3}$  M range). The reason why molecules having amino (primary or secondary) groups show better SERS activity in the gold sol is possibly due to the fact that these groups have the capability to be bound with gold nanoparticles. Binding of amines (such as hexadecyl aniline or alkyl amine) to gold nanoparticles is known<sup>27</sup>,

albeit relatively unexplored. To the contrary, molecules containing carboxylic acid functionality do not show enough response to SERS using the substrate. This is the reason why development of SERS-active substrates is always challenging and useful. No substrate is good for all types of compounds and whether a compound will be SERS-active or not depends on many factors. The micellar medium we used here might have some effect in this regard.

The intensity of SERS as tested with pyridine was strongly affected by the power of laser for excitation as observed by Sato<sup>28</sup>. At the low power, the intensity of Raman scattering was also low. However, at the higher power, the SERS intensity increased drastically.

A useful feature of the gold sol is the low background SERS signal. Figure 4e illustrates a blank spectrum for the photochemically prepared gold sol. No significant SERS or Raman bands from the surfactant are observed for the spectral region of interest.

From the studies made, it seems that the gold sol nanoparticles are especially good for the compounds containing aromatic amino group.

The results demonstrated the usefulness of the photochemically prepared gold sol nanoparticles as a practical substrate for SERS-detection. The sol is attractive because of its ease of production and the detection sensitivity that it offers with many SERS active compounds. The preparation does not need any expert hand. Since the sol has a selectivity feature, it may have the potential to be used as a substrate for the analysis of mixtures. Current efforts are being devoted towards extending the usefulness and applicability of this feature for chemical and biological analysis. More careful investigation and extensive studies with various other compounds are waiting to illustrate the behaviour of the sol towards SERS enhancement.

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## A SANS study on growth of anionic micelles with quaternary ammonium bromide

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**The micellar growth of sodium dodecyl sulphate in presence of inorganic (KBr) and quaternary ammonium bromides ( $R_4NBr$ ,  $R = C_2H_5$  or  $n-C_3H_7$ ) has been studied by small-angle neutron scattering measurements at 30°C. The data has been analysed using Hayter–Penfold model. After combining the results of previous and present studies, no direct relationship between length of alkyl part (R) and aggregation number ( $n_s$ ) of the micelles is found. It is proposed that both the inorganic and quaternary counterions (with  $R \leq C_2H_5$ ) cause micellar growth due to screening of micellar surface charge while latter ones (specially with longer R) do it by screening and increased hydrophobic interaction. Also,  $n_s$  increases with increase in  $[R_4NBr]$ .**

MICELLAR morphology is generally modified by the addition of suitable counterions<sup>1</sup>. Depending on their nature,

counterions may bind differently to the micelle and have important consequences on electrical double-layer, as well as for both inter- and intramicellar interactions<sup>2</sup>. Mostly, shape/size of the micelles depends upon the actual packing parameters in the assembly<sup>3,4</sup>. Many counterions/cosurfactants are strongly adsorbed at the micellar surface and, depending on the extent of penetration, this may change the mean distance between the polar head groups or increase the volume of the micellar core<sup>5–8</sup>.

Detailed accounts of sodium dodecyl sulphate (SDS) micelles in presence of simple inorganic counterions can be found in the literature<sup>9–16</sup>. As a rule of thumb, counterions having less affinity to water lead to higher binding to the micelles. This will have significant consequence towards micellar growth<sup>17,18</sup>. In contrast to inorganic counterions, quaternary ammonium ions ( $R_4N^+$ ) are essentially non-hydrated and amphiphilic<sup>14</sup>. In these ions the positive charge is buried in a paraffin shell. Interestingly, SDS micellar solutions show clouding in presence of such counterions<sup>19–22</sup>.

In our recent small-angle neutron scattering (SANS) measurements carried out on SDS- $R_4NBr$  ( $R = H, CH_3$  or  $n-C_4H_9$ ) systems<sup>23</sup>, one of the observations was that aggregation number ( $n_s$ ) of 0.3 M SDS micelle increased with all the salts (at 0.1 M).

In the present investigation, the effect of presence of inorganic and quaternary ammonium ( $R_4N^+$ ) counterions on the growth behaviour in 0.3 M SDS micellar solution has been investigated. Motivation of the work mainly came from the fact that these two types of counterions can influence the behaviour of micellar surface region with the concomitant influence on the SDS-micelle.

For this purpose we have performed SANS experiments on 0.3 M SDS-micellar solutions with different inorganic and  $R_4NBr$  salts.

SDS was the same as used in earlier studies<sup>8,23</sup>. Tetraethylammonium bromide (> 99%) and tetra-*n*-propylammonium bromide (> 99%) were obtained, respectively, from BDH (England) and Merck-Schuchardt (Germany). KBr (> 99%) was obtained from E-Merck (India). The salts were dried and stored as detailed elsewhere<sup>24</sup>. Solvent  $D_2O$  of 99.4% purity was supplied by the Heavy Water Division, Bhabha Atomic Research Centre (BARC), Mumbai.

The measurements were performed on the SANS spectrometer at CIRUS reactor, BARC<sup>25</sup>. The experiments used incident neutrons of mean wavelength ( $\lambda$ ) 5.2 Å with sample-to-detector distance 1.8 m. The angular distribution of the scattered neutrons was recorded with a one-dimensional position-sensitive detector. Under the present experiments, the data were recorded in the wave vector transfer ( $Q$ ) range of 0.02–0.3 Å<sup>−1</sup> ( $Q = 4\pi \sin\theta/\lambda$ , where  $2\theta$  is the scattering angle). The data for  $Q \geq 0.2$  Å<sup>−1</sup> are not shown as the signal-to-background ratio was very poor.

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