

observable by use of bright field illumination with high contrast for highly accurate measurements of sizes and shapes. The instrument includes a source of collimated light coupled to an afocal beam expander and an imaging array of photodetectors. When dust particles travel through the collimated beam, they cast shadows. The shadows are magnified by the beam expander and relayed to the array of photodetectors.

Inasmuch as the images captured by the array are of dust-particle shadows rather than the particles themselves, the depth of field of the instrument can be large: the instrument has a depth of field of about 11 mm, which is larger than the depths of field of prior particle-image velocimeters. The instrument can resolve, and measure the sizes and velocities of, particles having sizes in the approximate range of 1 to 300  $\mu\text{m}$ .

For slowly moving particles, data from two image frames are used to calculate velocities. For rapidly moving particles, image smear lengths from a single frame are used in conjunction with particle-size measurement data to determine velocities.

*This work was done by Brent Bos of Goddard Space Flight Center. For further information, contact the Goddard Innovative Partnerships Office at (301) 286-5810. GSC-15230-1*

## Enhancing SERS by Means of Supramolecular Charge Transfer

Sensors based on this method could detect chemical and biological hazards.

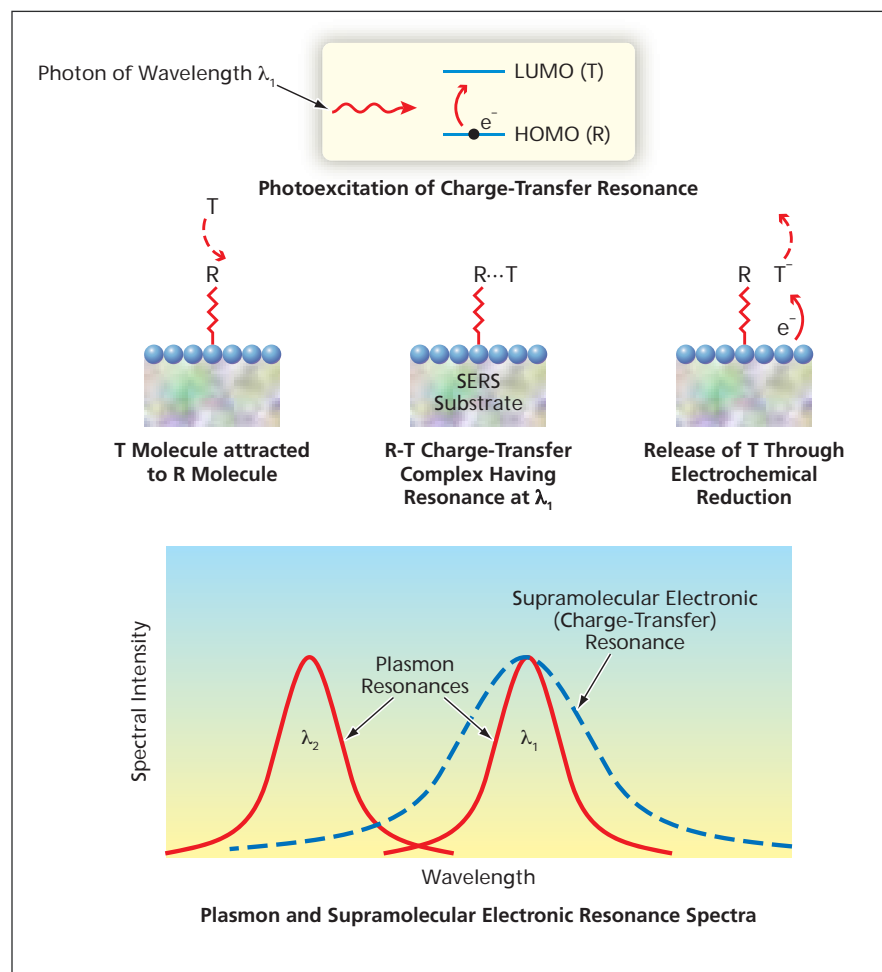
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In a proposed method of sensing small quantities of molecules of interest, surface enhanced Raman scattering (SERS) spectroscopy would be further enhanced by means of intermolecular or supramolecular charge transfer. There is a very large potential market for sensors based on this method for rapid detection of chemical and biological hazards.

In SERS, the Raman signals (vibrational spectra) of target molecules become enhanced by factors of the order of  $10^8$  when those molecules are in the vicinities of nanostructured substrate surfaces that have been engineered to have plasmon resonances that enhance local electric fields. SERS, as reported in several prior *NASA Tech Briefs* articles and elsewhere, has remained a research tool and has not yet been developed into a practical technique for sensing of target molecules: this is because the short range (5 to 20 nm) of the field enhancement necessitates engineering of receptor molecules to attract target molecules to the nanostructured substrate surfaces and to enable reliable identification of the target molecules in the presence of interferants.

Intermolecular charge-transfer complexes have been used in fluorescence-, photoluminescence-, and electrochemistry-based techniques for sensing target molecules, but, until now, have not been considered for use in SERS-based sensing. The basic idea of the proposed method is to engineer receptor molecules that would be attached to nanostructured SERS substrates and that would interact with the target molecules to form receptor-target supramolecular charge-transfer complexes wherein the charge transfer could be photoexcited.

As shown schematically in the figure,



A Target Molecule Would Become Bound to a receptor molecule on an SERS substrate. The resulting R-T complex would have a charge-transfer energy band that would coincide with a plasmon resonance,  $\lambda_1$ , of the substrate. Optionally, the target molecule could be released through electrochemical reduction.

a SERS substrate would be functionalized with a receptor (R) molecule that has an affinity for a target (T) molecule. The receptor molecule could be designed so that the lowest unoccupied

molecular orbital (LUMO) of the target molecule would lie above the highest occupied molecular orbital (HOMO) of the target molecule by an energy difference that would correspond to one of

the plasmon resonances of the SERS. Conversely, the plasmon of the SERS substrate could be tailored so that its resonance would lie in the charge-transfer energy band of the R-T complex. In addition to the aforesaid factor-of- $10^8$  SERS enhancement, there would be an additional enhancement, by a factor of the order of  $10^3$  to  $10^6$ , contributed by the vibronic energy levels associated with the charge transfer.

With this further enhancement, the detection principle is a form of surface enhanced resonance Raman scattering (SERRS) spectroscopy. The resulting Raman spectrum would consist of a mixture of SERS vibrational peaks from R

and T as well more intense SERRS peaks associated with R and T modes that participate in the charge transfer. These strong charge-transfer peaks would enable discrimination of important target molecules from interferants that may also be SERS-active. The sensor/molecule system as described thus far would potentially be reversible in the sense that the R-T interactions could be turned off by applying a bias voltage to electrochemically reduce T to T<sup>-</sup>. Because T<sup>-</sup> would no longer have an affinity for R, T could be easily washed away.

*This work was done by Eric Wong of Caltech, Amar Flood of the Indiana University Bloomington, and Alfredo Morales of Sandia*

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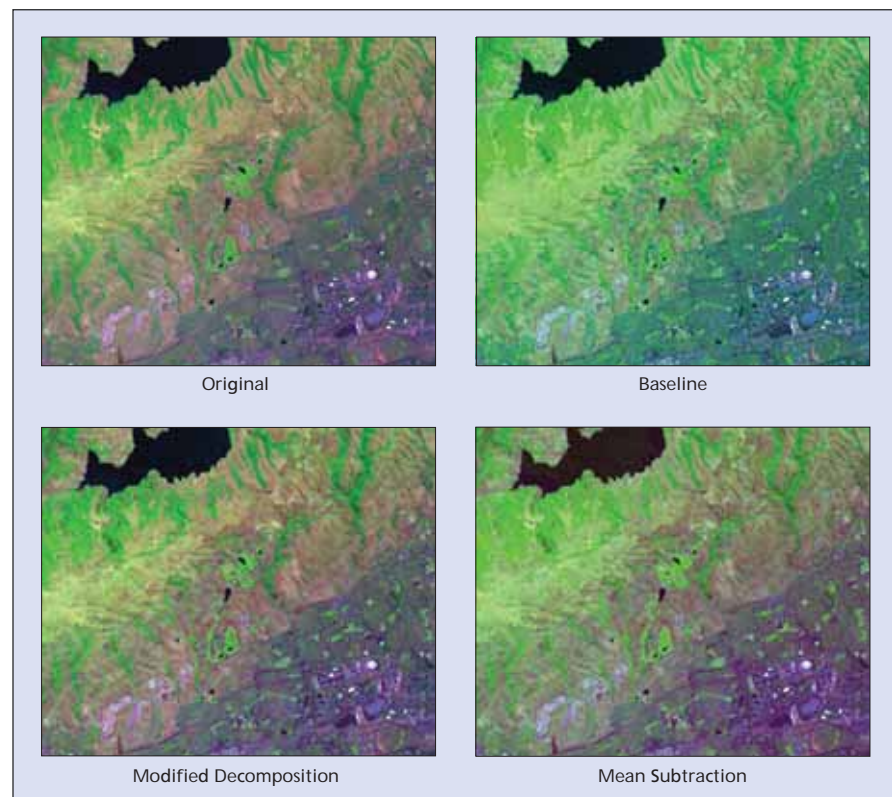
## Improving 3D Wavelet-Based Compression of Hyperspectral Images Detrimental effects of spectral ringing are reduced or eliminated.

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Two methods of increasing the effectiveness of three-dimensional (3D) wavelet-based compression of hyperspectral images have been developed. (As used here, "images" signifies both images and digital data representing images.) The methods are oriented toward reducing or eliminating detrimental effects of a phenomenon, referred to as spectral ringing, that is described below.

In 3D wavelet-based compression, an image is represented by a multiresolution wavelet decomposition consisting of several subbands obtained by applying wavelet transforms in the two spatial dimensions corresponding to the two spatial coordinate axes of the image plane, and by applying wavelet transforms in the spectral dimension. Spectral ringing is named after the more familiar spatial ringing (spurious spatial oscillations) that can be seen parallel to and near edges in ordinary images reconstructed from compressed data. These ringing phenomena are attributable to effects of quantization. In hyperspectral data, the individual spectral bands play the role of edges, causing spurious oscillations to occur in the spectral dimension. In the absence of such corrective measures as the present two methods, spectral ringing can manifest itself as systematic biases in some reconstructed spectral bands and can reduce the effectiveness of compression of spatially-low-pass subbands.

One of the two methods is denoted mean subtraction. The basic idea of this



These false-color **Images of Terrain** at Moffett Field, California include an original image formed from three spectral bands and three different similarly-formed versions as reconstructed after 3D wavelet-based compression of the original image to 0.1 bits/sample.

method is to subtract mean values from spatial planes of spatially low-pass subbands prior to encoding, because (a) such spatial planes often have mean values that are far from zero and (b) zero-mean data are better suited for com-

pression by methods that are effective for subbands of two-dimensional (2D) images. In this method, after the 3D wavelet decomposition is performed, mean values are computed for and subtracted from each spatial plane of each