- The release of heat in combustion of heptane is modeled adequately.
- A simplified, low-dimensional chemistry model depends on an adequate representation of a reduced rate set. The net constituent rate is nearly quasi-steady and can be split into an incubation zone of modest temperature rise followed by a fast-reaction zone of high temperature.
- The incubation region is characterized by reaction times of the order of milliseconds — similar to diffusion time scales. Therefore, chemistry is expected to be significantly coupled with flow processes during incubation. This coupling gives rise to several issues that must be resolved in further development of a simplified model.
- In the fast-reaction zone, the coupling between chemistry and flow processes is weak, and combustion is determined primarily by the mixing rate. The temperature profiles in the fast-reaction zone tend to be independent of the details of behavior during incubation.

The development of the model is not yet complete. To close the model system of equations, it will be necessary to determine effective mean source strengths for light molecules and light radicals resulting from decomposition of heavy molecules. The final model will thus focus on reactions of the light species; the necessary rates are expected to be well determined insofar as kinetic interactions among light species prevail.

This work was done by Josette Bellan and Kenneth Harstad of Caltech for NASA's Jet Propulsion Laboratory. Further information is contained in a TSP (see page 1). NPO-44750

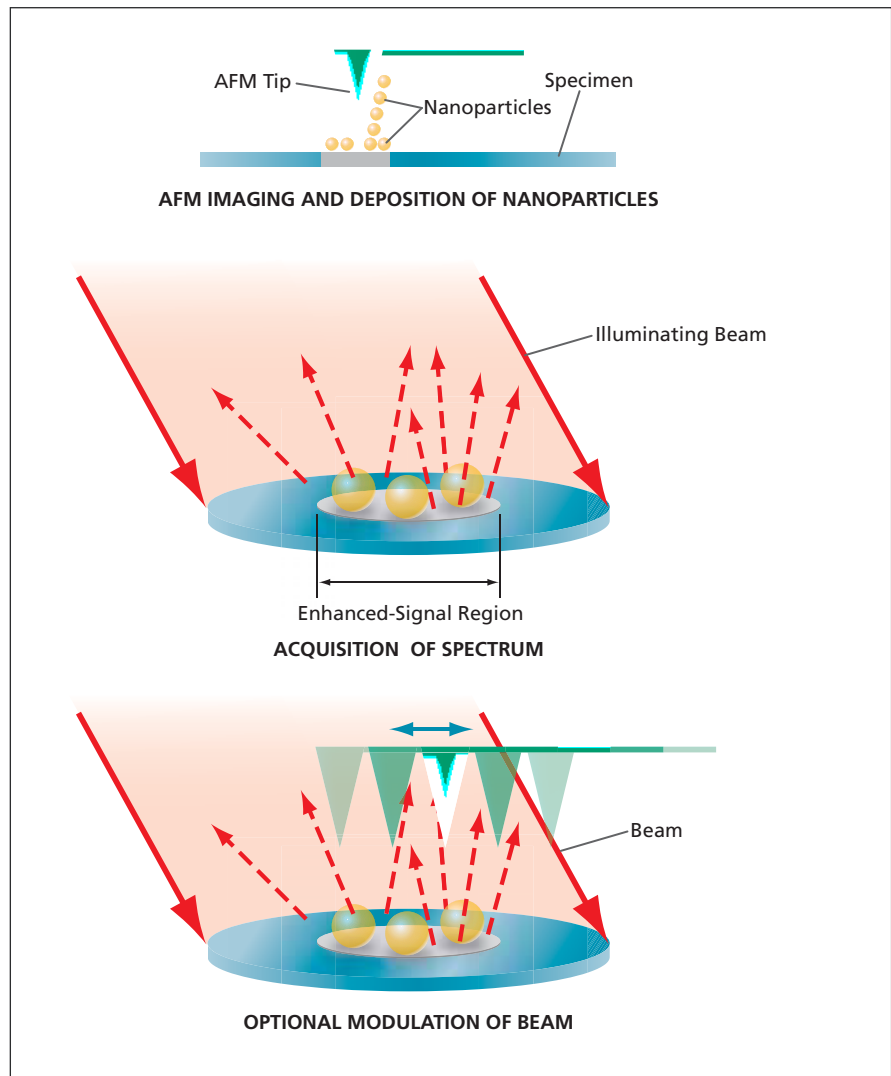# Near-Field Spectroscopy With Nanoparticles Deposited by AFM

It is not necessary to integrate an AFM with a spectrometer.

NASA's Jet Propulsion Laboratory, Pasadena, California

An alternative approach to apertureless near-field optical spectroscopy involving an atomic-force microscope (AFM) entails less complexity of equipment than does a prior approach. The alternative approach has been demonstrated to be applicable to apertureless near-field optical spectroscopy of the type using an AFM and surface enhanced Raman scattering (SERS), and is expected to be equally applicable in cases in which infrared or fluorescence spectroscopy is used.

Apertureless near-field optical spectroscopy is a means of performing spatially resolved analyses of chemical compositions of surface regions of nanostructured materials. In apertureless near-field spectroscopy, it is common practice to utilize nanostructured probe tips or nanoparticles (usually of gold) having shapes and dimensions chosen to exploit plasmon resonances so as to increase spectroscopic-signal strengths. To implement the particular prior approach to which the present approach is an alternative, it is necessary to integrate a Raman spectrometer with an AFM and to utilize a special SERS-active probe tip. The resulting instrumentation system is complex, and the tasks of designing and constructing the system and using the system to acquire spectro-chemical information from nanometer-scale regions on a surface are correspondingly demanding.

In the present alternative approach, unlike in the prior approach, one does not integrate a spectrometer with the AFM; that is, the spectrometer and the

AFM IMAGING AND DEPOSITION OF NANOPARTICLES

ACQUISITION OF SPECTRUM

OPTIONAL MODULATION OF BEAM

An **AFM Tip Is Used** to both image a specimen surface and deposit gold nanoparticles at a location of interest on the surface. Optionally, the tip can be moved through a spectrometer beam to modulate the light.

AFM are separate instruments. Moreover, instead of using a special SERS-active AFM/spectrometer probe tip, one fabricates SERS-active regions at locations of interest on the specimen surface by using an AFM tip to deposit gold nanoparticles at those locations.

The first step is to image the specimen by use of the AFM to establish the locations of interest for high-resolution spectro-chemical analysis. Then SERS-active regions are fabricated at those locations by a form of dip-pen nanolithography: The AFM tip is dipped into a colloidal gold solution and used to de-posit a single gold nanoparticle or a cluster of gold nanoparticles at each affected location (see figure). Then the AFM is disengaged, the deposited nanoparticles are illuminated in the spectrometer excitation beam, and the locally enhanced spectrum is acquired. Optionally, the AFM tip or the cantilever on which it is mounted can be moved above the deposited nanoparticles to modulate the light to enhance discrimination between the particle-enhanced components of the signal and the components from illuminated areas surrounding the particles.
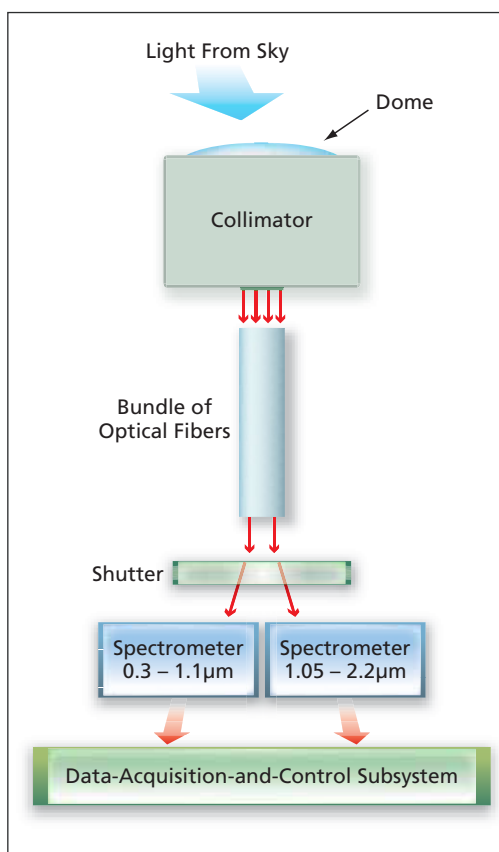
Light Collimator and Monitor for a Spectroradiometer
This system handles the optical input and electronic output of two spectrometers.

Ames Research Center, Moffett Field, California

A system that comprises optical and electronic subsystems has been developed as an infrastructure for a spectroradiometer that measures time-dependent spectral radiance of the daylight sky, in a narrow field of view (having angular width of the order of 1°) centered on the zenith, in several spectral bands in the wavelength range from 0.3 to 2.2 µm. This system is used in conjunction with two commercially available monolithic spectrometers: a silicon-based one for wavelengths from 0.3 to 1.1 µm and a gallium arsenide-based one for wavelengths from 1.05 to 2.2 µm (see figure). The role of this system is to collect the light from the affected region of the sky, collimate the light, deliver the collimated light to the monolithic spectrometers, and process the electronic outputs of the spectrometers.

This system includes a dome that faces the sky. Light collected via the dome passes through a collimator that has an aperture diameter ≈22 mm, a focal length ≈50 mm, and a field-of-view angular width that is adjustable between 1° and 2°. The collimated light enters a bundle of optical fibers that are chosen to have small numerical apertures so as to further limit the acceptance angle of received light. After propagating along the bundle of optical fibers, the light encounters a shutter that is operated on a controlled cycle, during which the shutter is alternately open for a time t_1, then closed for a time t_2. The cycle frequency can be 5 Hz or any suit-

The **Spectroradiometer** comprises optical and electronic subsystems that include two spectrometers operating in conjunction with the system described in the text.

able lower frequency; in practice, the cycle frequency (and, hence, the associated sampling frequency) is typically chosen to be 1 Hz.

When the shutter is open, light enters the monolithic spectrometer, electronic circuits in the spectrometers pre-process the outputs of photodetectors (one photodetector for each wavelength band), and the outputs of the spectrometer electronic circuits for the various wavelength ranges are sent to a data-acquisition-and-control subsystem that is part of the present system. When the shutter is closed, the same process takes place, for the purpose of collecting dark-current readings from the photodetector of each wavelength band.

The data-acquisition-and-control subsystem digitizes the spectrometer outputs and further processes them to generate any or all of a variety of useful output data. Among other things, this subsystem subtracts shutter-closed (dark-current) readings from shutter-open readings to obtain corrected spectral-radiance readings. In addition to alternately opening and closing the shutter and taking dark-current readings during the t_2 portions of successive cycles, the system can be made to sample dark currents during longer periods (e.g., a dark period of 5 minutes during each hour) to enable identification of anomalies in this system and/or in the spectrometers.