Progress Report (October 1, 1990 to September 30, 1991)

Laboratory. We moved into our new laboratory, in the just completed new Chemistry Building, in May 1991 (unfortunately a year behind schedule). This lab has the necessary anti-vibration (air-legged) optical tables, the necessary electrical requirements (680 volts, 60 amp), cooling water, air-handling, etc. requirements. There we were finally able to put together our super-microscope, consisting of a commercial inverted optical fluorescence microscope (Olympus), at the center of which is our home-built near-field scanning optical microscope (NSOM) described below. Adjacent, and connected via optical fibers, are a general use visible-ultraviolet cw laser (Spectraphysics, 30 w) and a single-mode He-Cd laser (Lyconix). Also adjacent is a laser (CO₂, 30 w) controlled micro-pipette pulling apparatus, optimized for optical-fiber nanotip fabrication (the only other such facility is at ATT, to the best of our knowledge). Next to that is our home-built specialized metal-coating facility. Next-door are: (1) our "standard" spectroscopy lab, containing two one-meter double-grating spectrometers and liquid-helium cryostats; (2) our "wet-lab", containing specialized crystal-growing, spin-coating, chemical purification and preparation, etc. facilities. While there are a specialized computer-control and imaging interface (RHK) and five dedicated microcomputers in the Super-Microscopy and Spectroscopy Labs, there is also a special adjoining room for computer analysis (DEC 5000, Microvax II, Mc-Intosh, IBM PC, etc.), with Ethernet connections to the nearby Chemistry Department computing facility (Silicon Graphics, etc.) and the University of Michigan Computing Center (IBM mainframe and supercomputer).

Photon and Exciton Tips. (1) We developed subwavelength, nano-pipette light sources, containing photo-stable crystal tips. We believe that this is an absolute first in the field. These are based on specially developed mixed organic
crystals (where the mixture is significantly more stable than each of its component crystals), molecularly doped polymers (another specialty of our group) and exploratory materials donated to us by dye industries (propriety). We also developed special chemical cleaning procedures which are a must for the successful metal-coating of the tip (a notorious problem). Combined with our own, specially constructed metal-coating facility (see above), we are now able to produce coated tips with no photon leaks (a one part per billion photon leak is inadmissible), while preserving at the same time an unobstructed orifice of about 50 nanometers in diameter. These nano-tips have been used in our scanning work (see below). A color figure (Fig. 1) is attached.

(2) We produced acceptable versions of silica nano-tips, pulled from single-mode optical fibers by an unpublished procedure just developed at ATT. This gives us an alternative to glass nano-pipette tips, which should improve the photon-flux by four or more orders of magnitude. An SEM photo of a metal-coated tip is attached (Fig. 2).

(3) We have developed composite crystal tips, where a crystal nanotip is coated with a nearly molecular layer of another crystal (e.g., anthracene with perylene). The latter acts as an energy concentrator (playing the role of the active center in a photosynthetic antenna). This solves three problems: a. photostability, b. tunable wavelength, and c. spatial resolution.

Samples. A number of special samples have been prepared. (1) Coated nuc1epore membranes. These were our early test samples (see below). Commercial ("Nuclpore") membranes with various pore-sizes were metal-coated and scanned both by electron-microscopy (SEM) and our near-field scanning optical microscope (NSOM). The results are given below. (2) Monomolecular crystalline films (e.g., perylene) on glass and other substrates were prepared by spin-coating. These samples are used as standards for Z-axis exciton microscopy and feed-back
measurements. (3) DNA "Star" samples have been prepared and tagged by fluorophores. A minor change of fluorophore is still needed to make these samples usable for our NSOM and Exciton-Microscopy. (4) Fluorescently tagged Langmuir-Blodgett films are also under investigation to provide us with finer calibration.

**Supermicroscope.** Our first version of combined NSOM and Exciton Microscope has been designed and constructed from scratch (while waiting for the new lab) and interfaced with the inverted fluorescence microscope (Olympus), the lasers (see above) and the STM imaging electronics (RHK) and computers (ACME, Easy-Data). It is schematically described in Figure 3. It has been operated successfully with many light tips (see below).

**Supermicroscope Scans.** We found it easiest to calibrate our scanning microscope with standard nuclepore membranes, coated with aluminum. The same membrane could be first scanned in vacuum in an electron microscope (SEM) and then in our table-top optical set-up. Figure 4 is an SEM scan. Figure 5 is our optical super-microscope scan (in NSOM mode). This demonstrated that the spatial resolution is indeed defined by the size of the light source (a 250 nm tip gives a 200 nm resolution). We have just reached a resolution of 100 nm and are moving fast on all fronts.

**Personnel and Summary.** In addition to the senior investigators, three postdoctoral workers (part-time), three graduate students (Applied Physics, Chemistry and Biophysics, (part-time) and three undergraduate students (part-time) were involved. Furthermore, we have some additional voluntary involvement in this project (due to its excitement): Profs. D. Axelrod (Biophysics), J. Moore (Organic Chemistry), R. Zenobi (Chemical Physics visitor from Lousanne) and Dr. Z. Y. Shi (Physical Chemistry). It’s due to everybody’s efforts that our project is on schedule, despite the crippling delay in Lab construction (see above) and a cardiac episode of the principal investigator. We also feel that our work has been
instrumental in pushing forward the entire field of optical supermicroscopy. The PI is also the organizer of the first ever NSOM and exciton microscopy meeting (Los Angeles, January '92, SPIE—The International Society of Photon Imaging Engineers).

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Figure Legends

Figure 1. A recent example of our exciton light sources. An aluminum coated nanopipette with a perylene crystal at tip. Excited by ultraviolet (350 nm) line of argon laser. Magnification about x1000. Note that the large yellow blob is due to overexposure (fastest camera setting).

Figure 2. A scanning electron microscope (SEM) picture of our new generation of nanoscope tips: An aluminized single mode optical fiber, produced with a micropipette puller, in which the platinum filament was replaced with a heating beam from a 25 watt infrared (CO$_2$) laser.

Figure 3. Schematic representation of the "heart" of the Ann Arbor Optical and Exciton Nanoscope. Scale 1:1. This "heart" was designed, constructed, assembled and tested out in our lab. It is located in the center of an inverted optical microscope ("Olympus"), of which only the objective is shown. The electronics and computer-graphics are slightly modified STM equipment (from RHK).

Figure 4. An SEM scan of an aluminum coated "Nuclepore" polycarbonate membrane. To be compared with Fig. 5.

Figure 5. A preliminary near-field optical microscopy scan of a "Nuclepore" polycarbonate membrane; resolution is approximately 200 nm.
Figure 1
Figure 3
Figure 4
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