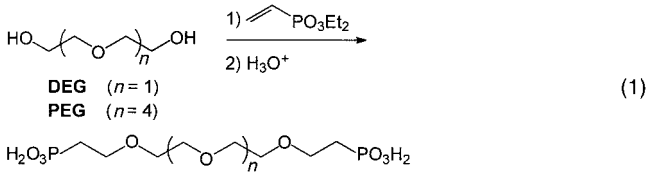
Experimental Section

The DEG and PEG diphosphonic acids were prepared by Michael-type double addition of the corresponding diol to diethyl vinyl phosphonate and final acid hydrolysis of the resulting tetraethyl phosphonic diester [Eq. (1)].



(1)

The pillaring procedure was performed by first exfoliating γ-ZrP (0.5 g) in water/acetone (1/1, 60 mL) at 80 °C. This dispersion of exfoliated lamellae was then mixed with a 0.015 M solution (20 mL) of DEG or PEG bisphosphonic acids in water/acetone (1/1) at 80 °C overnight.

Average values from elemental analysis and ^{31}P NMR spectroscopy[10] were used to determine the composition of the solids. Water content was derived by thermogravimetry with a Stanton STA750 thermoanalyzer. The interlayer distances were taken from the first reflection in the XRD patterns.

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[1] G. Alberti in *Comprehensive Supramolecular Chemistry*, *Vol. 7* (Ed.: J. M. Lehn), Pergamon, **1996**, chap. 5.
[2] A. Clearfield in *Progress in Inorganic Chemistry*, *Vol. 47* (Ed.: K. D. Karlin), Wiley, **1998**, pp. 373 – 510.
[3] M. B. Dines, P. M. Di Giacomo, *Inorg. Chem.* **1981**, *20*, 92 – 97.
[4] G. Alberti, U. Costantino, R. Vivani, P. Zappelli, *Angew. Chem.* **1993**, *105*, 1396 – 1398; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1357 – 1359.
[5] G. Alberti, F. Marmottini, S. Murcia-Mascarós, R. Vivani, *Angew. Chem.* **1994**, *106*, 1655 – 1658; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1594 – 1597.
[6] E. Brunet, M. Huelva, R. Vázquez, O. Juanes, J. C. Rodríguez-Ubis, *Chem. Eur. J.* **1996**, *2*, 1578 – 1584.
[7] G. Alberti, S. Murcia-Mascarós, R. Vivani, *J. Am. Chem. Soc.* **1998**, *120*, 9291 – 9295.
[8] G. Alberti, E. Giontella, S. Murcia-Mascarós, R. Vivani, *Inorg. Chem.* **1998**, *37*, 4672 – 4676.
[9] R. Begum, H. Matsuura, *J. Chem. Soc. Faraday Trans.* **1997**, *93*, 3839 – 3848.
[10] ^{31}P NMR (81 MHz, D_2O, 25 °C, 50 mg of sample dissolved in 1 mL of 2 M HF): $\delta = 28.7$ (m; PCH_2R), 0.6 (s; PO_4). Shifts are relative to 85 % D_3PO_4 in D_2O as external reference.

Laser-Induced "Regeneration" of Colloidal Particles: The Effects of Thermal Inertia on the Chemical Reactivity of Laser-Heated Particles**

Thomas E. McGrath, Andrew C. Beveridge, and Gerald J. Diebold*

Colloidal suspensions of metal particles frequently display surprising colors,[1, 2] the most striking examples being perhaps the deep red of colloidal gold and the light yellow-green of colloidal silver. Irradiation of colloidal carbon[3, 4] or colloidal metal solutions[5, 6] by a high-power, pulsed laser causes a reduction in the diameters and the dispersion of the suspended particles, resulting in dramatic changes in their optical properties that are easily discernible by the unassisted eye. We show here that the mechanism of change in several colloidal metal solutions involves rapid production of ions as a result of laser heating, followed by diffusion and chemical reduction on a long time scale to form new small-diameter colloidal particles. A result of the experiments is that large particles are differentially consumed relative to small ones. The recently reported method[7, 8] of forming colloidal suspensions through irradiation of solid metal surfaces submerged in water is also shown here to involve formation of ionic species.

When an aqueous suspension of particulate carbon, known as "India ink", is irradiated with a high-power, pulsed laser it rapidly becomes transparent as a result of carbon consumption through the carbon – steam reaction: Heating of the carbon particles on absorption of the laser radiation[3, 4] converts carbon and water into hydrogen and carbon monoxide, gradually reducing both the diameter of the carbon particles and the total amount of carbon in suspension. The recently reported observation of the same effect of size reduction in colloidal silver and gold suspensions[5, 6] suggests examination of the possibility of chemical reactions, albeit of an altogether different character than in the case of carbon in water, as playing some role in the mechanism of change. The first experiments carried out here sought to determine if Au^{3+} ions were generated by pulsed laser irradiation of a gold sol.

An aqueous suspension of gold particles of 100 nm diameter[9] has a surface plasmon resonance[1] at 566 nm, which is a result of collective oscillations of the electrons in small particles, giving the sol its distinctive color, as is evidenced by the absorption spectrum (inset of Figure 1). Irradiation of the suspension for 2 min at 10 Hz and 330 mJ per pulse with the unfocused output (532 nm, 15 ns) of a frequency-doubled Nd:YAG laser results in the formation of smaller gold particles, as is found from transmission electron microscope measurements[10] and as further evidenced in

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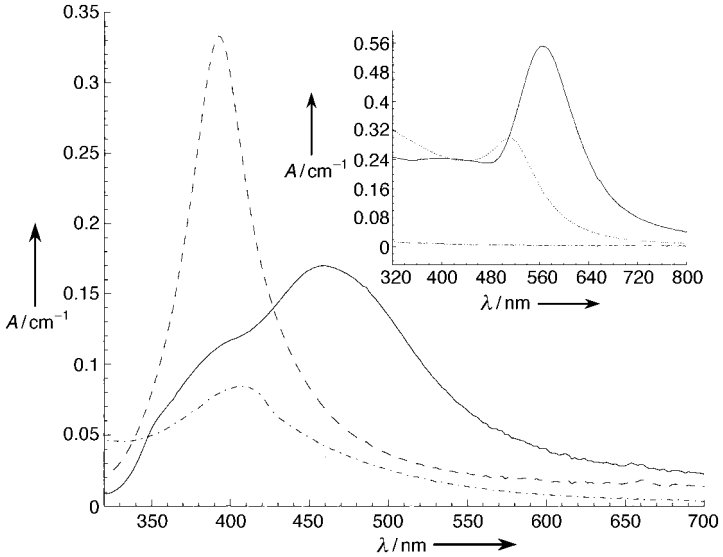

Figure 1. Optical absorbance A versus wavelength λ for a silver sol before irradiation (——), after irradiation (– – –), and after irradiation but with KI present (– · –). The I^- ion reacts with Ag^+ to form AgI. Inset: Optical absorbance versus wavelength for a gold sol before irradiation (——), after irradiation (····), and after irradiation with CN^- present (· – – ·).

Figure 1 by a shift of the plasmon resonance to 512 nm. Experiments to investigate the possibility of ion formation as a step in size reduction of particles employed $SnCl_2$, which acts as a color indicator for the presence of Au^{3+} ions. Following irradiation of a 0.2 mM sol of 100-nm gold particles, an equal volume of 2 mM $SnCl_2$ was added to the sol. The solution immediately turned to a deep purple color known as the "Purple of Cassius",[11] indicating a positive test for the presence of Au^{3+}. In a second experiment, CN^-, known to react with Au^{3+} to form $[Au(CN)_4]^-$, was introduced into a suspension of 100-nm colloidal gold particles before irradiation to determine the effect of scavenging Au^{3+} on the size-reduction process. A solution 1 mM in NaCN and 0.1 mM in colloidal gold was irradiated under the same conditions as in the previous experiment. The flat, featureless absorption spectrum taken after irradiation has neither of the plasmon resonances at 566 or 512 nm (inset of Figure 1), indicating consumption of 100-nm gold particles without the formation of new, smaller diameter colloidal particles. Similar experiments using Cl^-, which also scavenges Au^{3+}, gave absorption spectra devoid of peaks characteristic of gold surface plasmon resonances, again indicating that ion formation is an essential step in the mechanism that leads to size reduction of irradiated particles.

The particles of colloidal silver used in the experiments here,[9] as shown by transmission electron microscopy, were not uniform in diameter, or even, in general, spherical; the absorption of the sol is thus spread over a wide spectral region.[1] As shown in Figure 1, when such a silver colloid is irradiated with the frequency-doubled output of a Nd:YAG laser, the normally translucent solution, which has a broad, weak absorption from 350 to 550 nm, takes on a light green color that arises from a strong absorption of a surface plasmon resonance at 397 nm from particles with diameters on the order of 5 to 15 nm. Experiments analogous to those described above with gold were done with 26 mM silver sols using 2 mM I^- to precipitate any Ag^+ ions formed by absorption of laser radiation. Instead of showing a large increase in the absorption at the surface plasmon resonance at 397 nm after irradiation with 532-nm radiation, as is the case with neat silver sol, the suspension showed a decrease in absorption at 397 nm as well as a strong decrease in absorbance in the visible spectral region (Figure 1). Again, the profound effect of the presence of an anion that reacts with the metal cation of the colloid gives strong evidence that ion production is the primary route in the process of size reduction.

The time scales for destruction and reformation of the colloidal particles were also investigated. The absorption of the broad surface plasmon resonance of silver was monitored as a function of time after firing of the Nd:YAG laser using an Ar^+ laser probe beam (488 nm). The probe beam and the 532-nm beam were directed nearly colinearly into a 1-cm^2 cuvette. The decrease in absorption of the suspension at 488 nm (inset of Figure 2) takes place on a microsecond time scale and

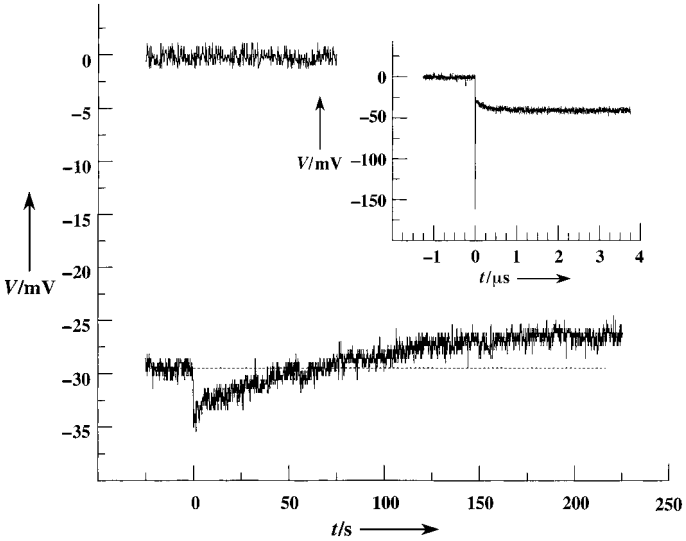

Figure 2. Lower trace: Phototodiode output voltage V versus time t showing the change in transmission of a silver suspension at 422 nm following irradiation of the cuvette with a single pulse of radiation (15 ns, 532 nm). Upper trace: Photodiode baseline taken with the probe laser beam blocked. The finite transmission of the solution before firing of the Nd:YAG laser, marked with a straight dotted line, can be attributed to scattering and absorption from large particles. Inset: Photomultiplier output voltage V versus time t showing the change in transmission of the broad continuum absorption in a silver suspension monitored at 488 nm following irradiation with 532-nm laser radiation. After the 330-mJ burst of 532-nm light, seen as a sharp spike at $t = 0$, the photomultiplier shows an increase in optical transmission.

corresponds to an overall decrease in absorption of the solution over a wavelength span of several hundred nanometers caused by reduction in the mean size of the particles. In a second experiment, the growth of the plasmon resonance at 397 nm was monitored by recording the absorption of a 422-nm probe laser beam. The initial decrease in absorbance of the suspension at 422 nm (Figure 2) can be attributed to a decrease in absorbance of the suspension over a wide wavelength span. The increase in absorbance corresponding to the formation of new particles takes place over a period of

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hundreds of seconds and can vary significantly depending on irradiation conditions such as the laser fluence and the number of shots fired. Analogous experiments carried out with a gold sol showed nearly identical time scales for the destruction and reformation of the gold particles. The results of these two experiments are consistent with a mechanism whereby metallic particles are partially converted into ions, which diffuse outwardly from the particles, and are later chemically reduced forming new small-diameter colloidal particles. The time evolution of the absorption of the surface plasmon resonance from the newly formed particles reflects a dynamic process as is typically seen in the chemical formation of colloids.[12, 13]

Transient grating experiments to investigate the time evolution of particles irradiated by intense laser radiation were carried out as well. In the transient grating technique[14] a laser beam is split into two equal-intensity beams that are recombined, giving an interference pattern in space with nodes and antinodes in the electric field. Formation of the interference pattern in a weakly absorbing liquid results in a sinusoidal deposition of heat in space. The result of the heat deposition is thermal expansion at the antinodal regions and the consequent launching of a standing acoustic wave, which owing to the density variations in the acoustic wave acts as a diffraction grating. The time evolution of the ultrasonic wave is typically recorded by directing a probe laser beam at the Bragg angle to the grating and recording the intensity of the diffracted light, which shows a waveform that varies with time and whose period is governed by the speed of sound in the fluid and the fringe spacing of the grating. Theoretical calculations[3, 15] have shown that the consumption of energy through chemical reaction results in what appears as a doubled frequency for the transient grating signal. The effect was first reported in carbon suspensions,[3] where the endothermic carbon–steam reaction is initiated by laser heating.

Transient grating experiments with colloidal gold showed a frequency-doubled signal for particles with diameters of 100, 40, and 20 nm, but not for particles with 5 nm diameter. With gold particles of 100 nm diameter, and the laser operating at 532 nm with an output of 50 mJ, a frequency-doubled signal was observed that diminished over the course of 250 laser shots, giving only the usual signal corresponding to the fringe spacing of the grating (Figure 3). On increasing the output energy to 200 mJ, the frequency-doubled signal reappeared, again gradually disappearing to give only the signal at the calculated frequency. The same effect could be initiated again by increasing the output energy to 330 mJ. The appearance of a frequency-doubled signal and its recurrence with increasing laser power suggests first that an endothermic reaction—namely, the desorption and ionization of atomic gold to produce Au^{3+} and three solvated electrons—is initiated by the laser heating, and, second, that the ability of the laser radiation to cause reaction depends on the laser fluence and the diameter of the particles in suspension. It is noteworthy that neither a suspension of gold particles with 5 nm diameter nor a filtered[16] carbon suspension gives a frequency-doubled signal; only a signal corresponding to the optical fringe spacing is seen.

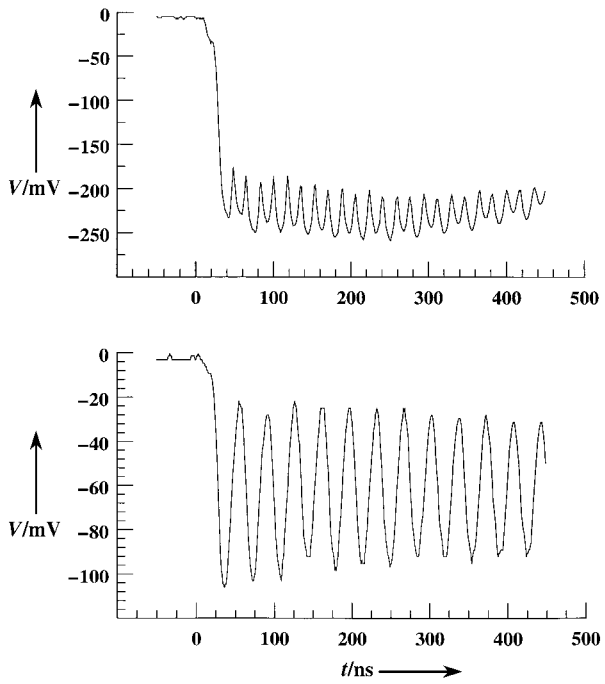

Figure 3. Photomultiplier output voltage V versus time t showing the evolution of the diffracted light signal. The initial transient grating signal (upper plot) decreases in amplitude and appears after 250-laser shots (lower plot) at the frequency corresponding to the optical fringe spacing of the grating.

The question of whether the process leading to ion formation is linearly related to the laser intensity was addressed by studying the formation of the plasmon resonance at 397 nm in silver sol by reducing the intensity of the laser but keeping the total amount of energy absorbed in the cell constant by increasing proportionately the number of laser shots. Experiments performed over a range of laser intensities using 532-nm radiation showed that an intensity threshold exists for changing the absorption spectrum of the colloid: A large number of low-intensity laser pulses is not equivalent to a small number of high-intensity pulses. Similar experiments done with gold sols gave the same result. These findings are consistent with a thermal mechanism of size reduction. Although the experiments do not delineate the details of the first step following absorption of radiation, it is likely that electrons are ejected[17, 18] from the particle surface, which in turn leads to ion emission and size reduction, the time scale for which depends on irradiation parameters. The presence of electrons following flash photolysis has been reported; however, the evidence is not incontrovertible.[19, 20] Hydrated electrons which would react on a short time scale, OH^- ions which reduce Ag^+ on a longer time scale and which are known to be formed by reaction of electrons with water,[21] are likely candidates as reducing agents.[13]

It has recently been shown that metal colloids can be produced by irradiation of bulk metal targets immersed in water using the 1.06-μm output of a Nd:YAG laser.[7, 8] Irradiation of a silver target with 700 mJ from an unfocused Nd:YAG laser produces a colloidal suspension whose absorption is easily visible to the eye after only a few seconds. Experiments conducted using an ion-selective electrode that

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responded to Ag^+ showed a strong ion signal after a few firings of the laser.[22] The presence of ions in the experiments with irradiation of bulk metal argues for the same final step in colloid production that is operative in the size reduction of colloids, namely, diffusion followed by chemical reduction and particle formation.

That the first step in size reduction is a thermal phenomenon is evidenced by a lack of any dependence of the reduction phenomenon on laser wavelength. Experiments with colloidal suspensions of C, Au, Ag, Pt, Fe, and Ni showed no significant difference in absorption spectra after irradiation for excitation at 355, 532, and 590 nm—all three wavelengths gave the same result.[23] From the theory of Mie scattering[1, 2] it is known that spherical particles whose diameter is smaller than the wavelength of the incident radiation absorb radiation and are heated uniformly throughout their volume. In the absence of any heat-loss mechanisms, such particles reach the same final temperature irrespective of their diameter. However, it can be shown[24] that when heat conduction takes place and when the time scale for heat conduction is commensurate with the laser pulsewidth, a particle that is large, but still smaller than the wavelength of the exciting radiation, is heated to a higher temperature and maintains that temperature longer than a small one. Large particles can be thought of as having a greater "thermal inertia" than small ones: For any heat-loss mechanism dependent on the surface area of the particle, large particles will maintain their temperature longer than small ones as a result of the volume-to-surface ratio, which increases as the first power of the radius. In the case of a polydisperse suspension of particles in a chemically reactive environment, a general principle for reactivity can be thus formulated: The largest particles in a laser-irradiated suspension, owing to their higher thermal inertia, reach a higher final temperature and maintain that temperature longer. They undergo chemical reaction to a greater extent than their smaller counterparts, giving, in effect, a size-dependent chemical reactivity. The failure of laser irradiation to effect changes in suspensions of small-diameter gold and carbon, the power dependence of the doubled frequency in the transient grating signals in colloidal gold, and the reduction in size and dispersity of large-diameter gold, silver, platinum, nickel, and iron sols can be explained by reactivity dependent on thermal inertia.

Although phrased somewhat differently in medical science, the above principle is clearly the operative mechanism in laser removal of, for instance, port wine stain, where large epithelial blood vessels are coagulated preferentially over small ones.[25] The application of the principle in experiments with metal sols clearly shows that the size and dispersity of colloidal particles can be controlled by irradiation with a pulsed laser. The size-reduction phenomenon itself is perhaps a first demonstration of the possibilities of laser manipulation of the physical or chemical properties of colloidal particles.

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[1] C. F. Bohren, D. R. Huffman, *Absorption and Scattering of Light by Small Particles*, Wiley-Interscience, New York, **1983**; the change in the Frolich frequency (which determines the color of the particle) as the particle diameter varies from 5 to 100 nm is discussed in Section 12.1.1; see also Section 12.4.1.
[2] H. C. van de Hulst, *Light Scattering by Small Particles,* Dover, New York, **1957**.
[3] H. X. Chen, G. Diebold, *Science* **1995**, *270*, 963 – 966.
[4] H. Chen, T. McGrath, G. Diebold, *Angew. Chem.* **1997**, *109*, 167 – 169; *Angew. Chem. Int. Ed. Engl*. **1997**, *36*, 163 – 166.
[5] A. Takami, H. Yamada, K. Nakano, S. Koda, *Jpn. J. Appl. Phys.* **1996**, *35,* 781 – 783.
[6] H. Kurita, A. Takami, S. Koda, *Appl. Phys. Lett*. **1998**, *72*, 789 – 791.
[7] J. Neddersen, G. Chumanov, T. Cotton, *Appl. Spectros.* **1993**, *47*, 1959 – 1964.
[8] A. Fojtik, A. Henglein, *Ber. Bunsen Ges. Phys. Chem.* **1993**, *97*, 252 – 254.
[9] The gold and silver suspensions were purchased from Ted Pella, Inc. Redding, CA.
[10] Transmission electron microscopic measurements carried out here corroborate the findings of ref. [6].
[11] N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements,* Pergamon Press, Oxford, **1984.**
[12] M. K. Chow, C. F. Zukoski, *J. Colloid Interface Sci.* **1994**, *165*, 97 – 109.
[13] Z. Huang, G. Mills, B. Hajed, *J. Phys. Chem.* **1993**, *97*, 11542 – 11550.
[14] H. J. Eichler, P. Gunter, D. W. Pohl, *Laser-Induced Dynamic Gratings,* Springer, Berlin, **1985**.
[15] H. X. Chen, G. J. Diebold, *J. Chem. Phys.* **1996**, *104,* 6730 – 6741. A frequency-doubled transient grating signal is predicted for endothermic chemical reactions, but has not yet been rigorously confirmed experimentally.
[16] Filtration of the carbon suspensions through a 0.2-μm filter is presumed to remove large carbon agglomerates, leaving individual particles.
[17] T. Linnert, P. Mulvaney, A. Henglein, *Ber. Bunsen Ges. Phys. Chem.* **1991**, *95*, 838 – 841.
[18] T. Linnert, P. Mulvaney, A. Henglein, H. Weller, *J. Am. Chem. Soc.* **1990**, *112*, 4657 – 4664.
[19] T. W. Roberti, B. A. Smith, J. Z. Zhang, *J. Chem. Phys.* **1995**, *102*, 3860 – 3866.
[20] P. K. Kamat, M. Flumiani, G. V. Hartland, *J. Phys. Chem. B* **1998**, *102*, 3123 – 2128.
[21] L. Onsager in *Modern Quantum Chemistry* (Ed.: O. Sinanoglu), Academic Press, New York, **1965**, pp. 123 – 128.
[22] Ag^+ ions were detected by the ion-selective electrode during irradiation of colloidal silver sols as well.
[23] Size reduction was determined by either transmission electron microscopy or by dynamic light scattering. Irradiation of colloidal silver at 355 nm did not give smaller particles; at this wavelength a photochemical pathway to form Ag_2O is open.[13]
[24] H. X. Chen, PhD thesis, Brown University, **1997**. Chen's calculations show the effect of heat conduction and laser pulsewidth on particle surface temperature for particles in the Rayleigh limit. The effect stated in the text must be obtained for any heat-loss mechanism dependent on surface area. Heat loss from laser-irradiated particles must include thermal conduction to the surrounding fluid and the production of phase transitions in the fluid surrounding the particles, both of which are proportional to the particle surface area.
[25] C. C. Dierickx, J. M. Casparian, V. Venugopalan, W. A. Farinelli, R. R. Anderson, *J. Invest. Dermatol*. **1995**, *105*, 709 – 714; M. J. van Gemert, A. J. Welch in *Optical-Thermal Response of Laser-irradiated Tissue* (Eds.: A. J. Welch, M. J. C. van Gemert), Plenum Press, New York, **1995**.

  1433-7851/99/3822-3356 $ 17.50+.50/0