Time-Dependent Reflection and Surface Temperatures during CO_2 Laser Irradiation of Dental Hard Tissues with 100-μs Pulses

Lasers, including CO_2 lasers operating around $\lambda \approx 10\ \mu$m, are being used frequently in dental soft tissue surgery and some dental hard tissue applications. In addition, pulsed CO_2 laser irradiation has been applied successfully for *in vitro* caries (dental decay) prevention or retardation.[1] For this application the laser is used for very localized surface heat treatment with or without inducing visible changes in the surface morphology.

For all laser applications to dental hard tissue the temperature increase in the pulpal region must be kept below ~4°C lest the pulp be damaged. If thermally induced modifications at or near the (enamel) surface are desirable while avoiding excessive subsurface thermal assault, it is advantageous to use a laser wavelength whose absorption length is very small, i.e., whose absorption coefficient is very large. For CO_2 laser radiation around 10 μm the absorption coefficients are very large[2] (see Fig. 62.50), ranging from ~5,000 cm^{-1} at 10.6 μm to 31,000 cm^{-1} at 9.6 μm, with corresponding absorption depths between 2 and 0.3 μm. These high absorption coefficients are due to intrinsic molecular vibrations of the phosphate ions (P–O stretching modes) of the mineral constituent (carbonated hydroxyapatite) of the dental hard tissue. Past research has found this region of the spectrum to be of particular interest for caries retardation.[1]

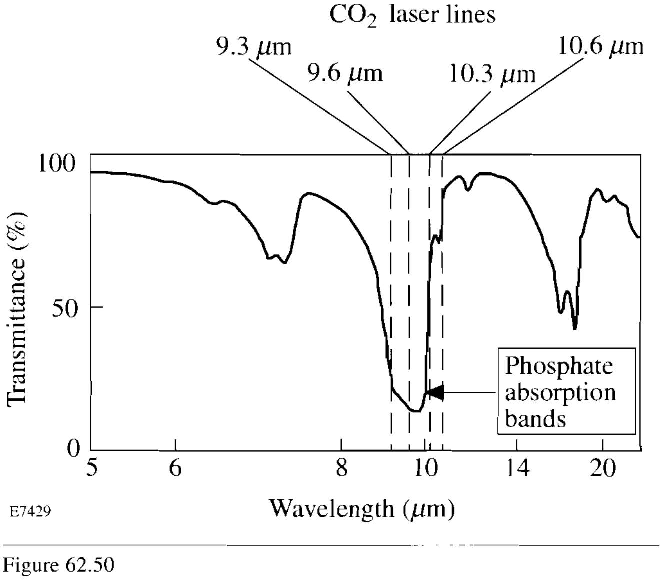

Figure 62.50
Absorption spectrum of dental enamel around the four major CO_2 laser lines. The absorption band in this region is due to vibrational bands in the phosphate bonds.

Pulses of appropriately short duration, in addition to short absorption lengths, are essential to avoid excessive subsurface heating. To avoid excessive heating at depths $\Delta x > 10\ \mu$m, one must choose pulse durations of the order of, or less than, the relaxation time ($\tau \approx \Delta x^2/4\kappa \approx 60\ \mu s$, $\kappa \approx 4\times10^{-3}\ \mathrm{cm^2/s}$ = thermal diffusivity) associated with this distance. While only approximate, these numbers are useful guides. Longer pulses or smaller absorption coefficients will heat thicker layers.

Very high absorption coefficients typically occur near resonances. All resonance transitions are typically temperature sensitive. For electronic transitions the peak absorption decreases with temperature while its width increases, but the resonance frequency remains constant. For vibrational resonances, S. S. Mitra[3] shows the temperature dependence of vibrational resonances in nonmetallic solids (e.g., MgO). The peak absorption coefficient drops rapidly between room temperature and ~600°C, and the absorption band broadens and shifts toward longer wavelengths. The frequency shifts are at least partly due to the lengthening of the bond distances. The resonances are typically asymmetric, and their shapes and values depend on the particular material.

Basic optics theory relates the absorption coefficient and index of refraction through the Kramers-Kronig relations.[4] The textbook index of refraction typically has a maximum on the long-wavelength side of the resonance and a minimum on its short-wavelength side. For vibrational transitions the behavior is qualitatively similar, though generally more complex. Nevertheless, as the temperature increases and the absorption decreases and shifts toward longer wavelengths, the index of refraction exhibits similar behavior, i.e., its peak values drop and the resonance broadens and shifts toward lower frequencies (longer wavelengths). We note that a similar temperature dependence of the strong absorption coefficient for water near $\lambda = 3$ μm has been reported in the literature.[5–7]

Associated with the index of refraction, n, is the well-known Fresnel reflection given by $R = (1-n)^2/(1+n)^2$. When the absorption coefficient is very strong (as it is typically near a resonance transition), the index of refraction becomes complex and can be written as $n = n_r + ik$, where n_r is the real part of the index of refraction, $i = \sqrt{-1}$, and k is the extinction coefficient. The extinction coefficient is related to the absorption coefficient by $\alpha = 4\pi k/\lambda$. Under these conditions the above Fresnel-reflection formula is rewritten as

$$R = \left[(1-n_r)^2 + k^2\right] \Big/ \left[(1+n_r)^2 + k^2\right]. \tag{1}$$

We note that for either n_r or k (or both) >> 1, the reflection coefficient approaches 100%! In fact, for enamel at $\lambda = 9.6$ μm we find $R \approx 50\%$, while for $\lambda = 10.6$ μm we find $R \approx 13\%$. These measurements were first reported by Duplain[2] for bovine enamel and have been verified in our laboratory for both bovine enamel and human enamel. Thus, if either k and/or n_r decreases due to their temperature dependence, the corresponding surface reflection decreases. While this observation certainly holds in the immediate vicinity of a resonance, farther away the reflection losses could actually increase with temperature due to the temperature dependence of the complex index of refraction.[2] The most dramatic changes in both n_r and k occur at rather modest temperatures below 600°C to 900°C with changes by factors of ≥ 2 being quite plausible.[3]

Since the surface temperatures during CO_2 laser irradiation can easily reach 1000°C or more, we can expect significant changes in the reflection coefficient during the laser pulse. Concomitant with a reduced reflection is increased energy coupling to the irradiated substrate; thus, the apparently paradoxical situation can arise where the absorption coefficient decreases while the absorbed energy increases, albeit over a greater volume.

In this article we report on time-dependent reflection and surface temperature measurements for laser-irradiated dental hard tissue at two of the four major CO_2 laser wavelengths (9.6 and 10.6 μm). These wavelengths were chosen for their potential usefulness in caries retardation if appropriate irradiation conditions are chosen.[1]

Method

Time-resolved reflection and surface temperature measurements were carried out using the experimental setup illustrated in Fig. 62.51. The light collector for the surface temperature measurements is an elliptical, rhodium-coated mirror (left side in Fig. 62.51) with an entrance hole at the top for the CO_2 laser beam. All thermal radiation emitted into the upper hemisphere was collected and imaged onto the HgCdZnTe detector, which has a time response of ~1 μs. The broadband filter shields the detector against scattered laser radiation and passes the thermal radiation between 5 and 9 μm. The signal from the detector was acquired by a digital oscilloscope (TEK2440) and recorded by a personal computer.

The time-resolved reflection measurements were made using a gold-coated integrating sphere as a light collector (right side in Fig. 62.51) with a broadband filter in front of the detector. The filter passes the laser light and adjusts the light level at the detector for optimum detection.

The recorded pyrometric signals were converted to surface temperatures using a calibration procedure described by Fried *et al.*[8] Synthetic carbonated hydroxyapatite (CAP) heated in a furnace at a known temperature of up to ~1000°C was employed as a calibration standard. A known area of the sample was imaged onto the detector using the same broadband filters as in the actual experiment. The results indicate that the emissivity is close to unity, i.e., the thermal emission from our samples is close to blackbody emission. However, we have no independent measurement of the absorption depths in the region between 5 and 9 μm. For the moment we assume that this absorption depth is small compared to the depths over which a given temperature is measured. This assumption is tenuous and must always be kept in mind when interpreting temperature measurements.

The strong temperature dependence of the total blackbody emission ($A\sigma T^4$, A = emitting area, σ = Stefan-Boltzmann constant, and T = absolute temperature) renders such a measurement insensitive to the exact value of A. Likewise, this strong temperature dependence strongly biases the measurement toward the peak temperature. Our actual measurements are carried out, however, in a fixed and limited wavelength interval (5 to 9 μm) causing the measured signal to follow a lower-power law (smaller exponent in T), which furthermore changes with temperature. While the calibration procedure takes this effect into account, the temperatures deduced from these measurements are more sensitive to the exact value of A

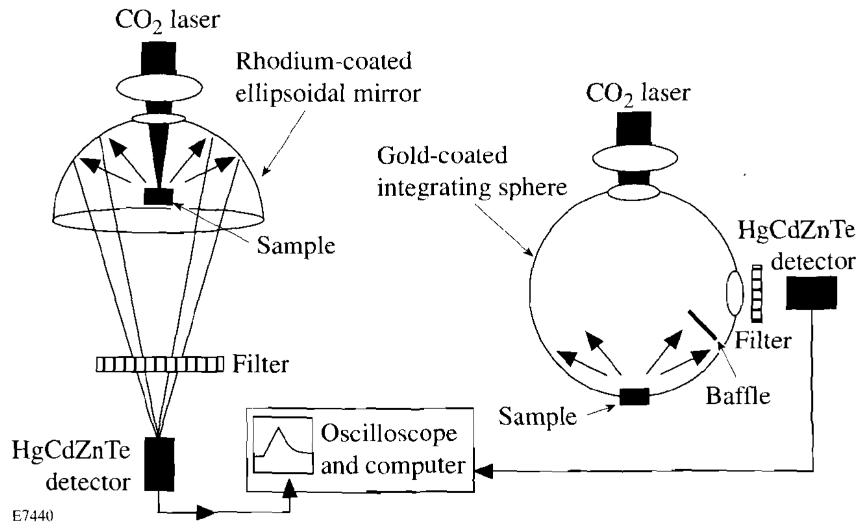

Figure 62.51
Experimental arrangement for measuring the time-dependent surface reflection (right side) and surface temperature (left side) of laser-irradiated dental hard tissue.

and less strongly biased to the maximum temperature in the area measured. As a consequence, assigning error bars to these measurements is rather difficult.

The tooth samples are unerupted, human third molars with a polished (1-μm grit size) enamel or dentin surface. The polished teeth are sonicated to remove the smear layer and polishing debris; the efficacy of this procedure is verified using scanning electron microscopy.

Our wavelength-tunable CO_2 laser (Pulsed Systems, Los Alamos, NM) is capable of delivering up to 200 mJ in pulses of 50 μs to 1 ms and is tunable from 9.3 to 9.6, 10.3, and 10.6 μm. At present we believe that the 100-μs pulse duration is the most suitable for caries retardation applications.

Results and Discussion

1. Time-Resolved Reflection in Dental Enamel

Typical time-resolved reflection measurements of human dental enamel are shown in Fig. 62.52 for $\lambda = 10.6$ and 9.6 μm. These wavelengths have the largest difference in absorption coefficient (see above) and therefore are expected to exhibit the largest difference in thermal behavior. For both wavelengths the reference pulse shown represents the reflection from an enamel surface irradiated at low fluence (~1 J/cm^2) scaled to 6 J/cm^2 (i.e., six times the reflected signal at 1 J/cm^2).

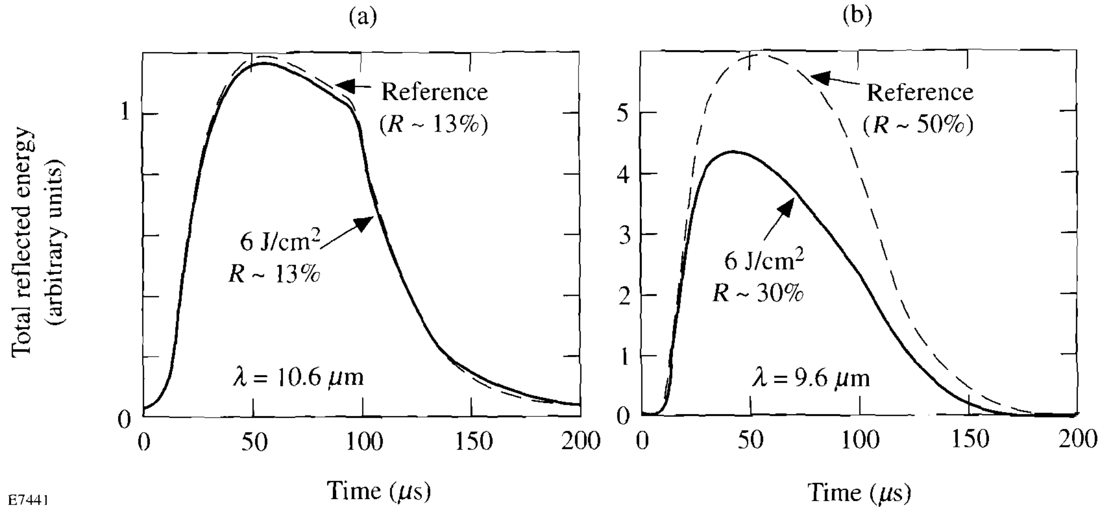

Figure 62.52
Time-resolved reflection from polished human dental enamel for two CO_2 laser wavelengths at low (~1-J/cm^2) and high (~6-J/cm^2) fluence. (a) $\lambda = 10.6$ μm, (b) $\lambda = 9.6$ μm. The reference (low-fluence reflection) is linearly scaled to that expected at high fluence and mirrors the incident pulse shape. The overall low-fluence reflections are ~13% and ~50% at 10.6 μm and 9.6 μm, respectively.

This reference is identical in shape to the incident laser pulse, implying no change in reflectivity during the pulse at that fluence. For the 10.6-μm reflection data [Fig. 62.52(a)] there is essentially no change in reflectivity as the fluence is raised from 1 J/cm^2 to 6 J/cm^2. In contrast, for λ = 9.6 μm [Fig. 62.52(b)] there is a very marked difference between the reflection signals registered for the two fluence levels. While the overall reflection loss at low fluence is ~50%, the reflection losses drop to ~30% at 6 J/cm^2; thus the amount of energy actually absorbed by the enamel increases at the higher fluence. These observations are consistent with the temperature-dependent absorption and reflection coefficients that are expected to decrease for the most highly absorbing CO$_2$ line at ≥6 J/cm^2, while remaining quite unaffected at 10.6 μm. At 10.6 μm the absorption is low and relatively far from the main vibrational resonances (see Fig. 62.50). On the basis of qualitative similarities with MgO we would expect no significant changes in either the absorption or reflection coefficient this far from the main resonance.[3]

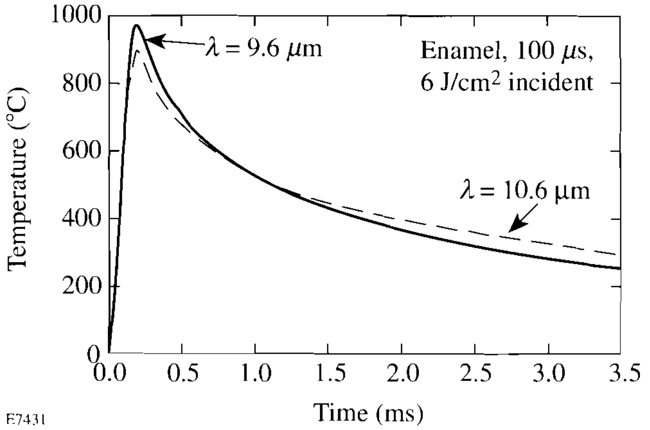

Figure 62.53
Time-resolved temperatures for enamel irradiated with 100-μs CO$_2$ laser pulses at 9.6 and 10.6 μm and a fluence of ~6 J/cm^2. The peak surface temperature for 9.6-μm irradiation is slightly larger than at 10.6 μm due to the higher absorption coefficient and in spite of the higher surface-reflection losses at this wavelength.

2. Time-Resolved Temperatures in Dental Enamel

Time-resolved temperature measurements show a great variety of behavior depending on whether enamel or dentin is irradiated and whether one looks at the first, second, tenth, or subsequent pulses.[9] At present we believe that these initial pulse-to-pulse changes in the temperature measurements relate to burnoff (blowoff) of the organic constituents of the dental hard tissue as well as some surface melting and recrystallization of the mineral substrate. After approximately ten pulses, the surface typically stabilizes, and temporal temperatures like those shown in Fig. 62.53 are obtained reproducibly. We note that for 9.6- and 10.6-μm irradiation with single, 6-J/cm^2, 100-μs pulses, the peak surface temperatures are quite similar for the two wavelengths with the peak surface temperature at 9.6 μm being slightly higher. The energy coupled into the sample is smaller by ~25% at 9.6 μm due to reflection losses (see preceding section). The deposited energy density near the surface is still larger, however, at 9.6 μm due to the higher absorption coefficient (shorter absorption depth)—even after allowing for the temperature dependence of the absorption coefficient and heat conduction into the interior of the target. The crossover of the two curves reflects the fact that at 9.6 μm less energy is deposited in the sample over a shorter distance than at 10.6 μm. This leads to higher surface temperatures at early times, while at later times, when thermal diffusion has heated a larger part of the sample, the detailed laser-energy deposition is unimportant and the measured surface temperatures reflect only the total energy deposited. We also note that at lower fluences (such as 4 J/cm^2) the temperature profiles for 9.6- and 10.6-μm irradiation of dental enamel are quite different, with 9.6 μm giving a markedly higher peak temperature.[9]

3. Time-Resolved Reflection in Dentin

The time-resolved, high-fluence (>6-J/cm^2) reflection from dentin surfaces exhibits a similar wavelength dependence to enamel. Here, too, we plot the time-resolved reflection after a number of pulses have stabilized the dentin surface. The reflection curves for prior shots are clearly affected by the blowoff of the organic constituents and water. After ~20 shots, scanning electron microscope (SEM) images at 60,000× magnification reveal a melted and recrystallized mineral surface devoid of organic material and quite like that obtained with enamel. All subsequent shots cause no further material blowoff from the surface as judged either optically or acoustically. Lower-magnification SEM images show differences between multiply irradiated dentin and enamel samples with, e.g., the dentinal tubules remaining open. The differences between the reference profile and the 6-J/cm^2 reflection profile at 9.6 μm [Fig. 62.54(b)] appear noticeably smaller than for enamel [Fig. 62.52(b)]. These differences largely disappear when one takes into account that the low-fluence reflectivity of irradiated dentin increases[9] from $R \approx 17\%$ to $R \approx 22\%$ after the dentin surface has been recrystallized by multiple irradiation at 6 J/cm^2. We therefore surmise that the basic absorption process is the same for irradiated enamel and dentin but the density of dentin near the surface is still somewhat lower than that of enamel. Under these conditions the overall absorption and reflection coefficients would be re-

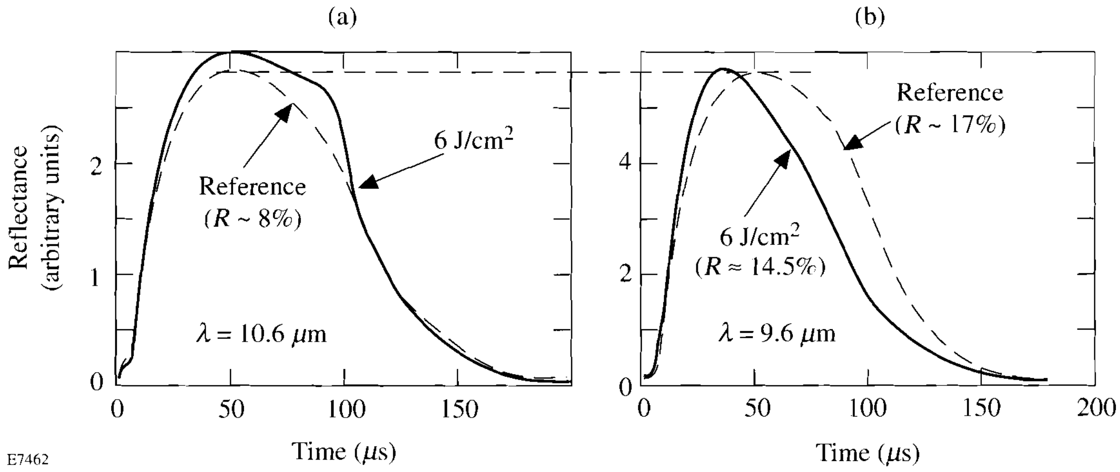

Figure 62.54
Time-resolved reflection from dentin irradiated at (a) 10.6 μm and (b) 9.6 μm. The reference pulse is the reflection at 1 J/cm^2 scaled to 6 J/cm^2 and is identical to the incident pulse shape. The strong wavelength dependence of the reflection at 9.6 μm is connected with the temperature-dependent absorption coefficient as in Fig. 62.52.

duced, but the relative change in reflection due to the temperature-dependent absorption coefficient would remain unchanged, consistent with our observations.

Conclusions

We have observed the first experimental evidence of time-dependent reflection in CO$_2$-laser-irradiated dental hard tissue at 9.6 μm, while no differences in reflectivity were observed at 10.6 μm. Using the known relationships between surface reflection and high absorption coefficients, we have related the reduced reflection for the high-fluence, 9.6-μm data to the temperature dependence of the absorption coefficient. This temperature dependence is much more pronounced in the immediate vicinity of the strong vibrational bands of the phosphate ions (9.6 μm) than farther away (10.6 μm). We have also seen direct evidence of this temperature-dependent absorption in time-resolved temperature measurements using fast photodetectors.

These data show that an appropriate choice of wavelength and pulse duration allows fine tuning of morphological surface modifications of irradiated dental hard tissue. Such fine tuning is expected to permit optimization of the laser-irradiation conditions for the purpose of caries reduction in dental hard tissue.

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