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Analysis of gas dispersed in scattering media

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Monitoring of free gas embedded in scattering media, such as wood, fruits, and synthetic materials, is demonstrated by use of diode laser spectroscopy combined with sensitive modulation techniques. Gas detection is made possible by the contrast of the narrow absorptive feature of the free-gas molecules with the slow wavelength dependence of the absorption and scattering cross sections in solids and liquids. An absorption sensitivity of 2.5×10^{-4}, corresponding to a 1.25-mm air column, is demonstrated by measurements of dispersed molecular oxygen. These techniques open up new possibilities for characterization and diagnostics, including internal gas pressure and gas-exchange assessment, in organic and synthetic materials. © 2001 Optical Society of America

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We demonstrate, for what we believe to be the first time, how free gas dispersed in scattering materials can be detected and characterized by use of diode laser spectroscopy. The technique, provisionally denoted gas in scattering media absorption spectroscopy (GASMAS) opens up new possibilities for characterization and diagnostics of scattering solids and turbid liquids.

Many substances, frequently of organic origin, are porous and contain free gas that is distributed throughout the material. For instance, wood, plants, fruits, cheese, powders, sintered materials, and foams can be considered. A common way to analyze gas *in situ* is to use absorption spectroscopy that employs a sufficiently narrow-band light source in combination with the Beer–Lambertian law. However, the straightforward application of this method fails for turbid media, since the radiation is heavily scattered in the material containing the gas. Thus there are no well-defined path lengths as required by the Beer–Lambertian law, but light emerges diffusely. This situation has been much discussed in connection with light propagation in living tissue, which has applications to optical mammography,[1–3] dosimetry for photodynamic therapy,[4] and concentration determinations for tissue and blood constituents.[5,6]

In this Letter we consider solid or fluid bulk materials containing pockets or small bubbles of gas. Light scattering is caused by inhomogenities in the optical properties of the medium. Even in the case of a clear liquid containing fine bubbles of gas, e.g., beer, a diffuse refraction occurs.[7] In the case of strong scattering, which is the most interesting aspect of the proposed gas-detection technique, a long effective path length is achieved, giving rise to a strong gas signature. Clearly, the gas-containing medium should not have substantial absorption of radiation in the wavelength range needed for monitoring of the particular gas. A consequence of this restriction is that materials containing liquid water, e.g., substances derived from living organisms, can be investigated only up to a limiting wavelength of $\sim 1.4\ \mu$m. Generally, absorption and scattering properties of solids and liquids have a very slow wavelength dependence. In contrast, free gas exhibits extremely sharp absorptive features. Thus bulk material will not influence the detected radiation when the frequency of a single-mode probing laser is slightly changed, whereas embedded gas gives rise to a tiny but narrow signal that can be picked up by use of modulation techniques even in the presence of a large background.

Diode lasers are particularly convenient sources of tunable radiation. Tunable diode lasers can easily be wavelength modulated by addition of an ac component to the driving current and are very suitable for monitoring of small but sharp absorptive features.[8] Modulation techniques can be used to increase detection sensitivity by typically several orders of magnitude compared with that of direct absorption.[9,10]

Two basic geometries can be considered when one is performing measurements with the proposed technique. In Fig. 1(a), a transillumination arrangement is presented, and in Fig. 1(b), a backscattering detection scheme is shown. In both cases optical fibers can be used for light injection and for collection of scattered radiation. In a medium with a homogeneous distribution of gas, the "history" of the photons

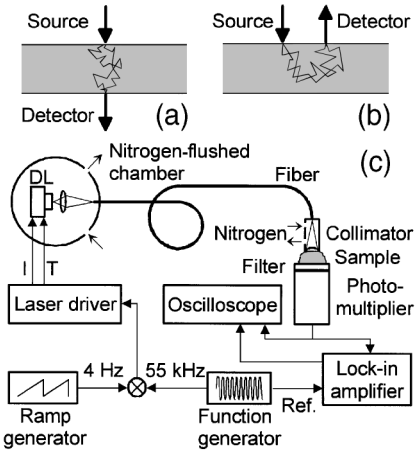

Fig. 1. (a), (b) Basic geometrical arrangements for monitoring of free gas in scattering media. (c) Experimental setup of the initial experiments. DL, diode laser; I, current; T, temperature control; Ref., reference.

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can partially be followed by measurement of the relative amplitude of the sharp gas-absorption signal, which increases with the path length. The absorption and scattering properties of the bulk material can be deduced independently by spatially resolved, time-resolved, or frequency-domain measurements, as is frequently done in tissue optics studies.[3] Thus a mean path length of the impinging photons through the scattering material can be estimated, which together with the magnitude of the gas absorption determines the concentration of the dispersed gas.

In our exploratory proof-of-principle measurements we used the setup shown schematically in Fig. 1(c). A tunable diode laser with a nominal wavelength of 757 nm at 25 °C and a free-running output power of 7 mW was used as a spectroscopic source for molecular oxygen monitoring. The spectroscopic measurements were performed on a double line near 759.95 nm ($R17Q18$ and $R19R19$) as well as on a strong isolated line at 761.003 nm ($R7R7$). These lines belong to the oxygen A band and were within the wavelength range of the diode laser that we used. Since oxygen is abundant in normal air, we placed the laser and a lens that focused the radiation into a 600-μm quartz fiber in a nitrogen-flushed chamber to eliminate spurious oxygen signals. At the other end of the fiber, the output light was collimated by another lens fixed in a nitrogen-flushed adapter. Since the transmitted light intensities through the samples were usually very low, it was important to ensure high detection sensitivity. Thus a photomultiplier tube with a 50-mm-diameter photocathode was used for detection. The ambient room light was effectively suppressed by a Schott RG695 colored-glass long-pass filter attached directly to the photocathode, in combination with the sensitivity falloff of the photomultiplier tube toward longer wavelengths. The samples were placed directly between the colored-glass filter and the collimating lens, which could be freely positioned by a fine translation stage. The diode laser was operated in a thermoelectrically cooled mount and was current and temperature controlled by a precision diode laser driver. Wavelength scanning was achieved by repetitive application of a current ramp with a repetition rate of 4 Hz to the drive current, whereas a sinusoidal current at 55 kHz was superimposed for wavelength modulation of the diode laser. The photomultiplier tube signal was picked up phase-sensitively by a lock-in amplifier. The extracted second-harmonic component and the direct signal were then accumulated for 256 scans in a digital oscilloscope.

Experiments were performed on a variety of samples of different thicknesses. Data for a piece of dried pine wood are shown in Figs. 2(a) and 2(b). Measurements were performed with the collimator lens of the transmitter initially in contact with the surface of the sample and then retracted to add several free air paths of well-defined lengths. The oxygen contained in the scattering medium could be evaluated as illustrated in Fig. 2(a) by use of the standard addition method, which is well known from physical chemistry. Since the absorption is of the order of a few percent, the signal is expected to depend linearly on the concentration. An equivalent mean path length in the sample, i.e., the mean distance that light travels through air dispersed in the sample, can be evaluated. For determination of the sensitivity of the oxygen concentration measurement, the specific absorption of oxygen was also measured in air with the laser beam strongly attenuated by a neutral-density filter. We also calibrated the wavelength-modulation signal by use of long-path direct absorption in air (measurable at a path length of 4.5 m), given the atmospheric oxygen concentration of 20.8%. In the present experiments we were able to detect an absorbance of 2.5×10^{-4}, which corresponds to a 1.25-mm column of air.

The signal that was due to oxygen dispersed in a 26-mm-thick slice of apple is displayed in Fig. 2(c), which shows that liquid water does not pose problems for measurement in this wavelength region. Finally, Fig. 2(d) shows signals from a bulk of turbid epoxy glue containing air bubbles embedded at an ambient pressure of 300 mbars. The pressure dependence of the line shape can clearly be seen, illustrating the potential of the technique for internal pressure assessment, e.g., in porous mineral samples or sintered ceramics. Measurement data for different samples are compiled in Table 1, in which the thicknesses of the samples are also given. Note that the evaluated air equivalent mean path lengths through the different samples are often several times longer than the geometrical dimension but can also be shorter, as in epoxy.

Our experiments show that it is possible to monitor small and sharp absorptive features that are due to free gas in strongly scattering solids by use of sensitive diode laser spectroscopy. Many applications of this new type of scattering spectroscopy for solids and

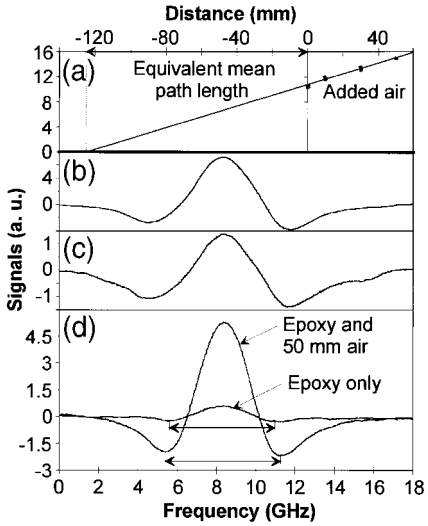

Fig. 2. Experimental data for lines in the molecular oxygen A band obtained by wavelength-modulation diode laser spectroscopy. (a) Standard addition plot for a 10-mm-thick piece of wood, (b) corresponding recorded line shape for wood only, (c) spectral recording for a 26-mm-thick slice of apple, and (d) spectra for a 19-mm-thick bulk of turbid epoxy containing air bubbles at low pressure and when 50 mm of background air is added. The isolated molecular oxygen line was used in these last two recordings.

Table 1. Equivalent Mean Path Lengths for Oxygen-Containing Porous Media of Various Thicknesses

Material	Thickness (mm)	Equivalent Mean Path Length (mm)
Wood	10	123
Apple	26	33
Lump sugar	12	20
Granulated salt	18	170
Wheat flour	18	380
Polystyrene foam	19	600
Turbid epoxy	19	5

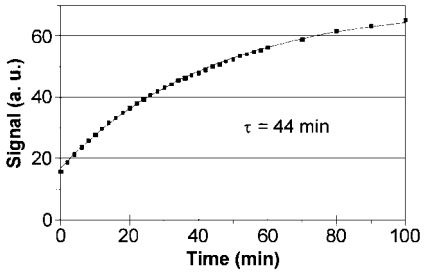

Fig. 3. Recording of the oxygen-signal increase of a 19-mm-thick piece of polystyrene foam while it is kept in ambient air but after it has been stored in a pure nitrogen atmosphere.

liquids can be envisaged. By use of these techniques it would be possible to monitor *in situ* physiological and degradation processes in various biological substances. Such measurements have been limited to extraction of emitted gas from, e.g., plants, fruits, and insects, measured by normal gas spectroscopic techniques.[11,12] The largest challenge would be to develop methods for monitoring minute amounts of free gas inside human tissue, possibly allowing development of new diagnostic techniques for diseases.

The new possibility of observing free gas in scattering media allows not only static gas assessment but also the study of dynamic processes, i.e., how embedded gas is exchanged with the environment. For instance, an object can be surrounded by a gas, and the successive gas penetration into the object can be studied. This example is demonstrated in Fig. 3. A piece of polystyrene foam was first subjected to a pure nitrogen atmosphere for 4 h. Invasion of oxygen into the material was observed to occur with a time constant ($1/e$) of 44 min. This experiment suggests that radioactive labeling can sometimes be replaced by the new technique.

In the limit of very small (nanometer-scale) enclosures of free gas, additional collisional broadening and shifts of diagnostic value can be expected. Note also that tomographic reconstruction of the gas distribution in the material is possible by use of multiple fibers placed around the object.

Quantifying and fully exploiting diagnostic aspects of gas in scattering media require full modeling of the multiple-scattering material. The theoretical and experimental techniques developed for medical applications are useful in this respect.[2,13] Time-resolved measurements are particularly powerful, providing a direct and independent assessment of photon history.[1,14,15]

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