Light emission of dental enamel after infrared resonant excitation

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Abstract

A visible emission of dental enamel has been observed after infrared excitation by pulsed CO_2 radiation well below the ablation level. The visible radiation can only be detected in narrow resonant frequency ranges of irradiation in the infrared which correspond to vibrational excitation in the stretch mode of the PO_4 group. The IR induced visible luminescence of dental enamel is investigated by spectrally and temporally resolved measurements. Possible mechanisms of energy transfer are discussed. © 1998 Elsevier Science B.V.

1. Introduction

Powerful pulsed infrared transversely excited atmospheric (TEA) CO_2 laser systems make it possible to study nonlinear effects as laser-induced multiphoton excitation (MPE) and dissociation processes of molecules [1]. The strong excitation of molecules under IR laser radiation leads to visible luminescence when the laser radiation frequency is tuned in resonance to the frequency of the vibrational modes [2,3]. The luminescence was identified as emission from electronically excited molecular dissociation products. This effect of multiphoton dissociation can be regarded to be nearly universal in polyatomic molecules and was demonstrated for several molecular gases.

Recently the emission of photons from a solid by a multiphoton excitation process through vibrational states was reported. Porous silicon shows visible luminescence after high-level vibrational excitation of the Si–O and Si–H_x absorption band [4–6]. Narrow resonances in the efficiency of light emission at 1030, 1084 and 2110 cm^{-1} with different spectral and temporal responses are found. The relaxation times are in the order of a few μs.

Oxygen-rich materials like dental enamel exhibit strong absorption bands in the infrared spectral region around 1000 cm^{-1} which correspond to the absorption bands of hydroxyapatite $(Ca_5(PO_4)_3(OH))$, the main constituent of dental

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enamel [7,8]. Application of the CO_2 laser in dentistry has demonstrated that surface changes and ablation of dental enamel can be produced which have a strong wavelength dependence [7–9]. These effects of the CO_2 laser on the tissue have recently been studied with scanning electron microscopy (SEM) and were attributed to the strong phosphate and carbonate absorption bands in dental enamel [10].

In this work, we report on the first observation of light emission of dental enamel excited by a pulsed CO_2 laser with intensities well below the ablation threshold [10–12]. Visible radiation is only observed at narrow resonances of excitation in the infrared which can be identified with vibrational modes of phosphate ions in dental enamel. The emission in the visible range is a highly nonlinear function of the infrared excitation intensity I_{IR}, being proportional to its sixth power. Temporally resolved luminescence and luminescence excitation spectra have been measured giving insight into the absorption processes which result in the emission of light.

2. Experimental

In our experiments, the extracted non-carious human teeth are mounted in a chamber evacuated to 1 mbar. Single high-power IR pulses of a TEA CO_2 gas laser tunable in discrete steps from 926 to 1088 cm^{-1} (9.2–10.8 μm) serve as radiation sources of the teeth. The pulse width is 150 ns in the primary peak, followed by a low intensity tail of about 1 μs. The pulse power of the incident IR pulses was controlled by inserting calibrated CaF_2 absorbers and simultaneously monitored by means of a calibrated fast photon drag detector [13]. A thick Ge window is used as a cut-off filter to suppress visible light in the excitation pulse. The luminescence of the teeth are spectrally and temporally resolved using a monochromator and a photomultiplier with a time resolution of 5 ns. The photoluminescence spectra are corrected for the spectral response of the optical system. The peak excitation intensities of a laser pulse given below are determined from the spot size of the laser beam on the sample and the maximum of the photon-drag detector signal.

3. Experimental results

We observe visible luminescence up to photon energies of 2.8 eV. For example, at a frequency of 1088 cm^{-1} this corresponds to the absorption of more than 24 incident IR quanta. The luminescence signal occurs only in a very narrow band of infrared excitation around 1088 cm^{-1}. In Fig. 1 we present an example of the time resolved study of the luminescence at a photon energy $E_{LUM} = 2.07$ eV. The dashed line gives the temporal profile of the IR excitation pulse at a frequency of the CO_2 laser of $\tilde{\nu} = 1088$ cm^{-1}. The strong luminescence signal rises throughout the period of the primary IR pulse and has its maximum after 1 μs. For increasing times the signal follows a mono-exponential decay with a time constant of 3.0 μs. The decay time exhibits an increase with increasing IR excitation intensity from 2 μs at 3 MW/cm^2 to 4 μs at 11 MW/cm^2. The temporal structure of the luminescence pulse is the same at all detection energies E_{LUM}. The visible luminescence is so high that it can be seen by the eye.

More specific information on the origin of the excitation process that leads to the luminescence is gained from the luminescence-excitation spectrum shown in Fig. 2. The emission intensity at $E_{LUM} = 2.07$ eV is plotted versus the frequency $\tilde{\nu}$ of the infrared excitation by scanning the lines of the CO_2 laser. The measurement shows that there is no luminescence in a wide range of excitation frequencies. A narrow resonance occurs at $\tilde{\nu} = 1084$ cm^{-1} followed by a strong rise of the luminescence intensity for frequencies higher than $\tilde{\nu} = 1086$ cm^{-1}. The structure of this second peak cannot be spectrally resolved as no emission lines of our CO_2 laser system are accessible for photon energies higher than 1088 cm^{-1}.

We would like to point out that previous investigations of the application of high power CO_2 lasers on teeth were concentrated on the ablation process at much higher fluences than here. Well above the ablation threshold sparking and thus visible radiation has been observed due to a white plume of hot plasma of ablated material [14] at an excitation frequency of 1042 cm^{-1} where no visible radiation could be detected in the present investigation at lower fluences.
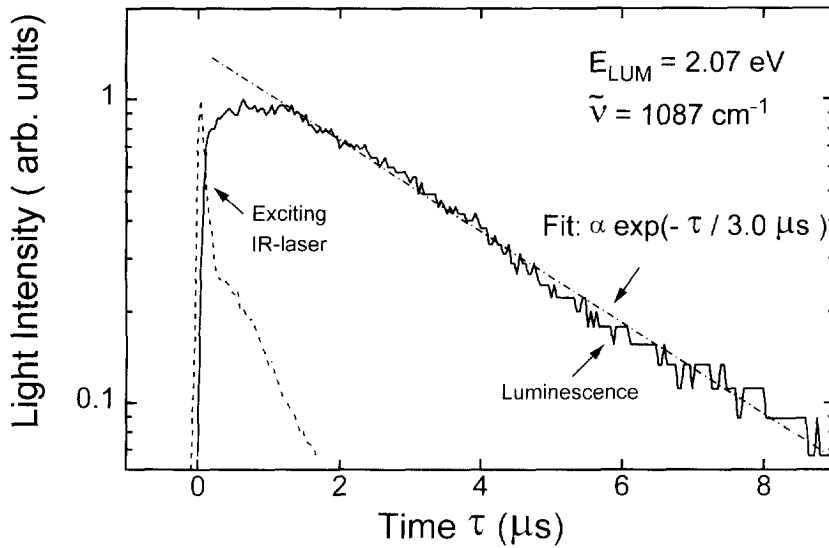
Fig. 1. Time evolution of the measured light emission from dental enamel after excitation at $\tilde{\nu} = 1088$ cm^{-1} ($I_{IR} = 6.8$ MW/cm^{-1}) by a CO$_2$-laser pulse (solid line). The detection energy was $E_{LUM} = 2.07$ eV. The dashed–dotted line represents a mono-exponential fit with a time constant of 3.0 μs. The temporal shape of the IR excitation pulse is given by the dashed line.

Dental enamel is a carbonated hydroxyapatite (Ca$_5$(PO$_4$)$_3$(OH)) containing 2–5 wt% carbonate, which is crystallographically disordered. The linear infrared spectrum of dental enamel contains bands due to each of the four phosphate internal vibrational modes ν_1–ν_4 and bands corresponding to the four

vibrational modes of the carbonate ion and the hydroxyl groups [7,8]. The intense absorption bands of hydroxyapatite coincide with the TEA CO$_2$ laser lines in the region from $\tilde{\nu} = 929$ to 1088 cm^{-1}.

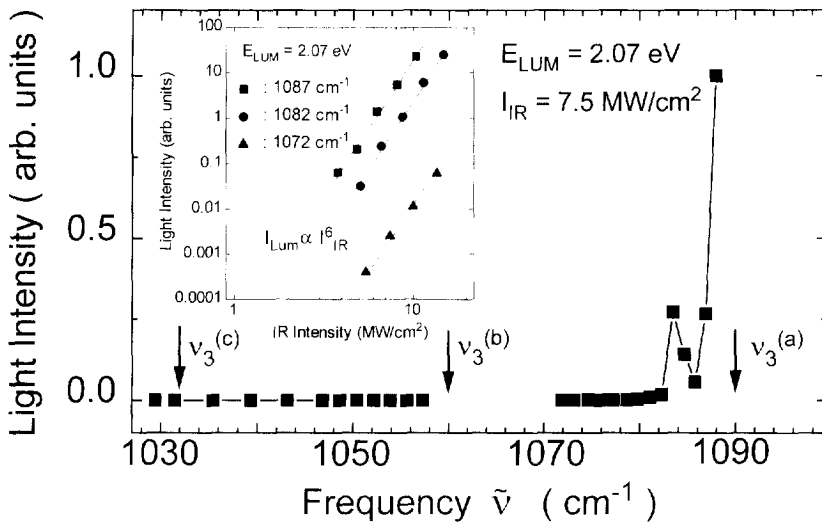The arrows in Fig. 2 indicate the position of the infrared active ν_3 vibrational modes of PO$_4$ in the

Fig. 2. Light intensity at $E_{LUM} = 2.07$ eV as a function of the IR frequency $\tilde{\nu}$. The arrow marks the spectral position of the ν_3(PO$_4$) transitions. In the range of 1058 to 1071 cm^{-1} measurements were not possible because of the gap between the two emission bands of the CO$_2$ laser. Inset: Magnitude of the luminescence signal versus IR pulse intensity at $\tilde{\nu} = 1072$, 1082 and 1087 cm^{-1} with $I_{LUM} \propto I_{IR}^6$.

present spectral range as determined from linear absorption measurements [7,8]. Different frequencies of the ν_3-mode are due to different possible crystallographic sites of PO_4 in apatite [7]. The $\nu_3^{(b)}$ mode at 1060 cm^{-1} is not accessible by the CO_2 laser due to the gap between 10 and 9 μm bands. Specially the intense rise of the luminescence intensity in the PLE spectrum for frequencies higher than $\tilde{\nu} = 1080$ cm^{-1} coincides with the highest transition frequency of the molecular vibration of the phosphate ion in carbonated hydroxyapatite at $\nu_3^{(a)} = 1090$ cm^{-1}. The lack of any luminescence of the $\nu_3^{(c)} = 1032$ cm^{-1} mode might be due to the fact that the corresponding crystallographic site is not present in our samples.

The strong dependence of the luminescence intensity on the IR laser intensity is illustrated in the inset of Fig. 2 for different IR excitation frequencies of the CO_2 laser. The luminescence rises nonlinearly with the excitation intensity, following $I_{LUM} \propto I_{IR}^6$ independently of the selected excitation frequency $\tilde{\nu}$. In our experiments, the selected laser intensities were well below the optical breakdown threshold. No significant surface changes have been observed on the sample. Light emission from a plume can be

ruled out due to the kinetics of radiation. The kinetic of the plume in response to CO_2 laser pulses has been investigated in detail by Fried et al. [14] showing a delay of the emission of 80 μs which is two orders of magnitude larger than observed here. Plasma emission can also be ruled out because the decay time of the observed luminescence is substantially longer than that measured at much higher power levels when sparking occurred. The kinetic of plasma emission generated by a Nd:YLF laser at 1.053 μm has been observed and characterized by Niemz [15,16] yielding decay times in the order of not more than several nanoseconds.

The spectral shape of the induced luminescence is given in Fig. 3 for several excitation densities at two different excitation energies of the CO_2 laser. Independently of the chosen excitation conditions a broad structureless luminescence spectrum is found which shows no wavelength dependence in the observed spectral region and no structures within the resolution of 3 nm. The IR induced luminescence differs substantially from the conventional luminescence of dental enamel after excitation with UV light. There, distinct luminescence peaks are found around 3.5,
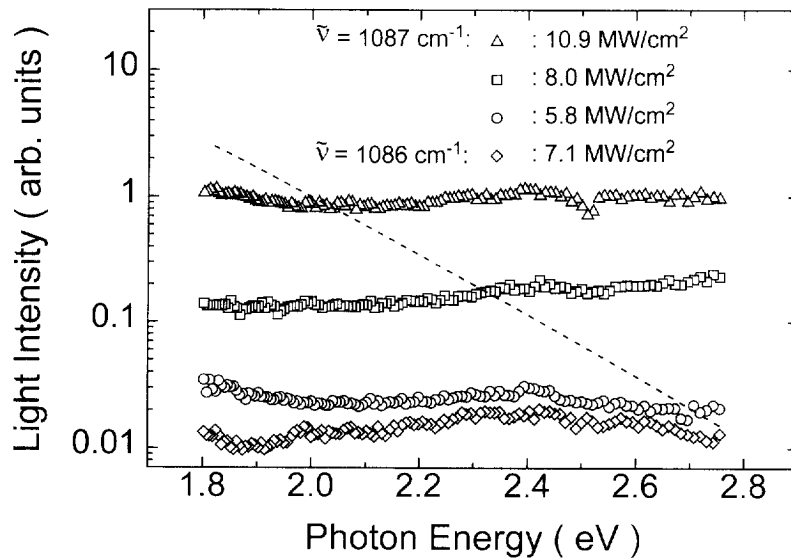

Fig. 3. Spectrally resolved luminescence after IR excitation at $\tilde{\nu} = 1087$ and 1082 cm^{-1} for several excitation intensities. The broken line represents the calculated drop of black-body radiation with an assumed temperature of 1200 K. The magnitude of the estimated thermal radiation is not in scale with the experimental data. The line should only allow a comparison of the spectral dependencies of thermal radiation and luminescence.

3.0, 2.8 and 2.2 eV [17,18]. The origin of the usual luminescence is presumed to be in the organic and inorganic components of the material.

4. Discussion

Different types of physical mechanisms can be considered which might lead to the origin of the emitted light. If we regard published surface temperature measurements, irradiation of dental enamel by CO_2 laser light with 100 ns pulse duration and absorbed fluences of 5 J/cm^2 per pulse at 1075 cm^{-1} leads to a surface temperature of about 1200 K [19,20]. This momentary temperature rise is sufficient for the rapid fusion and melting of enamel crystallites to take place [10]. In the present experiment the highest level of fluence was about ten times lower yielding a correspondingly much smaller temperature. Even if we assume a black-body light source with an effective temperature of 1200 K, the black-body Planck distribution would have a maximum at about 0.5 eV in the infrared and the characteristic exponential drop of the Boltzmann tail for higher photon energies by three orders of magnitude in the spectral range of Fig. 3. The slope of the drop of the calculated thermal radiation is plotted in Fig. 3 by the broken line. The magnitude of this radiation is estimated to be much smaller than the observed signals. In contrast to that, the observed emission spectrum is practically independent of photon energy in the measured spectral range. Thus, our measured luminescence data cannot be described by radiation heating of the sample. This conclusion is supported by measurements at even much higher fluences in the range of ablation where heating of the bulk material has also been ruled out [14].

Next, we discuss a multiphoton excitation process which seems to be responsible for the visible luminescence of dental enamel after intense IR excitation. The following explanation is based on a model for multiphoton excitation of vibrational levels of polyatomic molecules [2,3], which has recently been used to explain the light emission from porous Si after high-level vibrational excitation in the Si–O [4] and Si–H [6] absorption bands. The absorption of the IR photons by the stretching vibration of the PO_4 group leads to an excitation of low-lying resonant transitions which are discrete and anharmonic in nature.

This is accomplished due to compensation of the anharmonic frequency detuning of successive vibrational transitions because of changes in the molecular vibrational energy and anharmonic splitting of excited degenerate vibrational states. The density of states increases rapidly with energy because of the strong interaction of a large number of vibrational states. Above about the 3rd to 6th level of the excited modes the states become so dense that they form a quasi-continuum. In this regime instead of narrow resonances of multiphoton absorption a wide smooth band appears which allows a successive absorption of IR radiation. Further the high laser intensity induces power broadening of the levels, which reduces the frequency mismatch in the multiphoton absorption process. Hence under a rather high-fluence IR pulse a considerable fraction of vibrational excited PO_4 molecules can pass to an excited electronic state which allows the emission of visible light.

Successive excitation of the first few discrete vibrational levels of the phosphate ion in carbonated hydroxyapatite is responsible for the strong resonant character of the multiphoton excitation process around the $\nu_3^{(a)} = 1088$ cm^{-1} mode (see Fig. 2). The role of IR radiation intensity in excitation of lower vibrational levels depends substantially on the type of molecule which governs the value of anharmonicity, the character of splitting of each vibrational level and the position of the vibrational quasicontinuum. In the case of polyatomic molecules like PO_4, typically up to 6 IR photons should be absorbed until the quasicontinuum is reached [3]. These 6 stimulated transitions seem to account for the dependence of the luminescence intensity on the IR intensity, which follows a $I_{LUM} \propto I_{IR}^6$ dependence, if the IR excitation energy is tuned close to the resonance of the $\nu_3^{(a)} = 1090$ cm^{-1} mode (see inset of Fig. 2). Comparative experiments in porous Si after high-level excitation in the Si–O and Si–H stretch vibration have demonstrated similar results [4,6]. There too, the lifetime of the luminescence occurs on a μs timescale and the efficiency of light emission follows a I_{IR}^6 dependence. A drastically different behavior is monitored in the IR induced luminescence spectra. In porous Si, an exponential decrease of the spectral distribution of the light emission is found [4]. In contrast, our measurements in dental enamel show no wavelength

dependence of the luminescence in the observed spectral range (Fig. 3). This behavior is not yet understood, it might be due to a convolution of luminescence of hydroxyapatite and organic components in the material as it has been discussed with respect to UV-excited luminescence spectra [17,18].

5. Conclusions

In conclusion, the experiments presented here give the first observation of light emission from dental enamel at resonant excitation of PO_4 vibrational modes by CO_2 laser radiation at fluences well below the threshold of ablation. The excitation spectrum shows sharp resonances caused by the highly nonlinear multiphoton process. This allows one to precisely locate the center of broad absorption bands. The resonances are in fact in wavelength ranges which have been found to be optimal for ablation being important in dental surgery.

Acknowledgements

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