conformational change of the protein is one of the requisites of biological electron transport to be performed "one direction" by using a series of cytochromes, oxidases,[13] and reductases.[14] More importantly, the present significant information can be obtained only by the use of SFCD. Neither static CD nor electronic spectroscopy will suffice, since this abnormally enhanced CD comes from the rapid conformation change of the active site and/or the dynamic magnetic polarization induced chemically. This point is discussed in detail in a forthcoming paper.

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Iwao Tabushi,* Kazuo Yamamura, Takako Nishiya
Department of Synthetic Chemistry, Kyoto University
Yoshida, Kyoto 606, Japan
Received September 5, 1978

Pulsed Infrared Laser Induced Visible Luminescence

Sir:

Triboluminescence (TL) can be excited by fracturing or grinding a crystal, or by subjecting it to thermal shock.[1-3] We have been interested in whether comparable phenomena could be made to occur using a high energy laser pulse as the stress inducing agent. We report here on three cases in which there is luminescence induced by a 20-ns, 1060-nm pulse from a Nd glass laser system,[4] the pulse energies ranging from 0.5 to 4 J cm^{-2} (~200-MW peak power). The crystalline materials were doped saccharin (see immediately below), coumarin, sodium chloride, and potassium chloride. Individual crystals were used in each case; they were single crystal in appearance and several mm in each dimension. All were studied at room temperature, ~25 °C.

Figure 1A shows the laser induced luminescence spectrum for saccharin; it is the same within our resolution as the TL and photoluminescence (PL) spectra. The emission is actually from *p*-toluenesulfonamide impurity normally present in saccharin; such doped saccharin crystals are among the more intensely triboluminescent materials observed in our laboratory,[5] hence this initial choice. The laser induced emission (LIE) showed two time regimes, as followed at 480 nm: a prompt emission and a longer-lived one whose decay fit an exponential of ~300-ns lifetime. From separate optical excitation experiments, the 480-nm emission has a lifetime of 57 ps at 77 K. The prompt component of the laser induced emission could represent ordinarily decaying excited states, but the 300-ns component must have some other explanation, as discussed further below. The intensity of the 300-ns emission was proportional to the laser pulse energy over about a tenfold range.

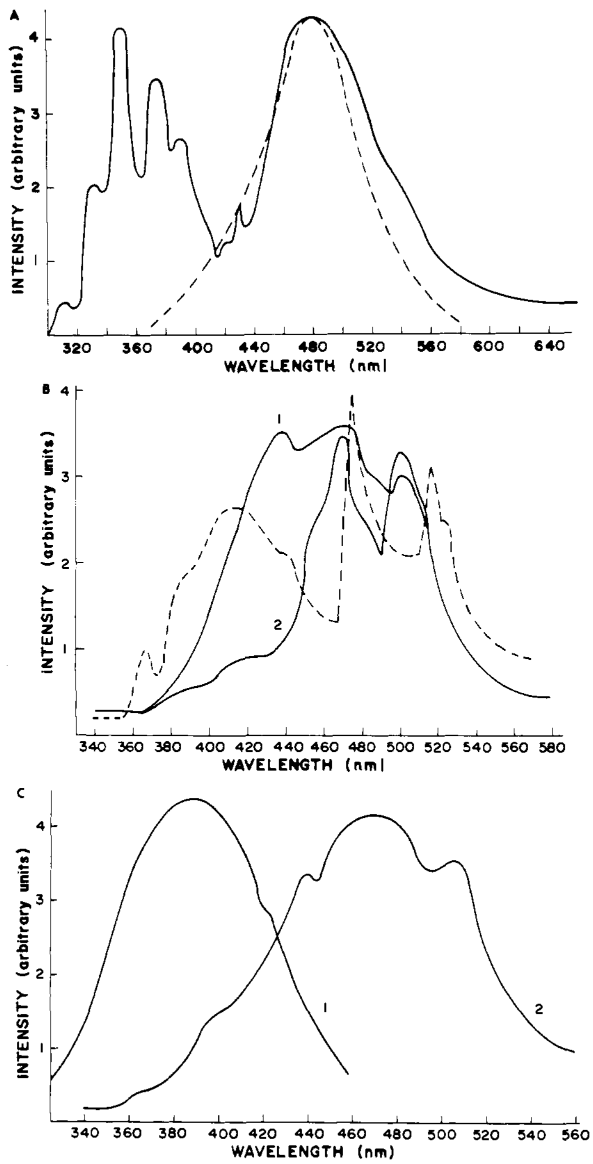

Figure 1. Spectra. (A) *p*-Toluenesulfonamide doped saccharin: full line, triboluminescence spectrum (the short wavelength, structured emission is due to excited state N_2);[6] dashed line, laser induced emission. (Both measurements at room temperature; the 480 nm peaks are normalized.) (B) Coumarin: full lines, laser induced emission, curve 1 with no delay, and curve 2 with 80-ns delay; dashed line, 353-nm photoexcited emission at 77 K (at room temperature, only the 420 nm centered emission is observed). (The intensity scale is arbitrary, and the spectra are roughly normalized; they are uncorrected.) (C) Laser induced emissions from NaCl, curve 1, and KCl, curve 2.

Substantial differences exist between the laser induced emission and TL spectra of coumarin. The LIE spectrum shown in Figure 1B consists of three peaks at 430, 475, and 505 nm. At room temperature, the PL and TL spectra of coumarin consist of a broad band centered at ~400 nm, which has been assigned as a $\pi \leftarrow \pi^*$ fluorescence.[7,8] At 77 K, the PL spectrum consists of the fluorescence and a highly structured phosphorescence. The LIE of coumarin most closely resembles

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the lower temperature PL spectrum, with the most prominent peaks at 474 and 505 nm arising from $\pi \leftarrow \pi^*$ phosphorescence. The time dependence of the peaks follows the expected behavior. As the delay time between the laser pulse and the LIE measurement was decreased from 80 ns to 0, the intensity of the fluorescence at 430 nm increased relative to that of the phosphorescence.

The laser induced emissions of NaCl and KCl consist of broad bands centered around 380 and 470 nm, respectively, as shown in Figure 1C. Neither crystal is photoluminescent with visible or UV excitation, or triboluminescent in this spectral region. However, X- or γ-ray irradiated crystals show both TL and thermoluminescence.[9] The emission is due to recombination of displaced electrons with lattice atoms or ions. The emission spectra vary with crystal preparation and history, and with excitation method and temperature. Thus for NaCl, reported emission maxima range from 350 to 420 nm, and those for KCl, from 400 to 440 nm.[9,10] Our laser induced emission match the above characteristics.

Certain trivial explanations of our observations can be ruled out. Ordinary photoluminescence can be eliminated, of course, on energetic grounds, nor is there any evidence for PL via higher harmonic generation. Neither 530- nor 353-nm scatter was observed. Also, successive multiphoton absorption can be eliminated in the case of saccharin since the emission intensity was linear in laser pulse energy.

We can suggest two possibly important mechanisms: mechanical stress and electron-hole recombination. It is known, for example, that laser pulses such as used here can produce pressure waves reaching kilobar levels.[11-13] A possibility, then, is one of laser shock induced triboluminescence. This could be the case with the doped saccharin. The spectra of the LIE and TL molecular emissions are essentially the same. The 300-ns emission decay in the former case is about what would be expected were a fan of shock-induced stress concentrations, or of actual cracks, propagating through the crystal at the speed of sound (with attenuation). The crystals all tended to crack or spall on successive laser shots. Note, however, that the laser induced emission differs from triboluminescence in that no excited-state N_2 emission occurs.

The mechanical stress explanation also suffers in the case of coumarin since the TL spectrum shows only molecular fluorescence, while the LIE shows both fluorescence and phosphorescence. The cases of NaCl and of KCl are quite clearly unrelated to triboluminescence—there is none giving such emissions. Thus laser shock induced mechanical stress waves may account for some of the observations, but not for all of them.

Surface effects, such as the production of surface plasma may play a role in the excitation.[12] The intense laser beam could produce electron-hole pairs and an associated pressure or heat wave might then induce electron recombination with consequent emission. Although the mechanism is uncertain at present, our results clearly indicate that intense IR pulses can excite molecular fluorescence, molecular phosphorescence, and alkali metal halide defect emission.

The phenomena are under continuing investigation. Preliminary indications are that pulsed laser induced emission occurs with other crystalline materials. A partial list includes $BaPt(CN)_4$, europium(III) chelates, uranyl nitrate, phenanthrene, phthalic anhydride, and chlorotriphenylmethane.

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G. E. Hardy, B. P. Chandra, Jeffrey I. Zink*
Department of Chemistry
University of California, Los Angeles
Los Angeles, California, 90024

Arthur W. Adamson,* Robert C. Fukuda, R. T. Walters
Department of Chemistry, University of Southern California,
Los Angeles, California, 90007

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