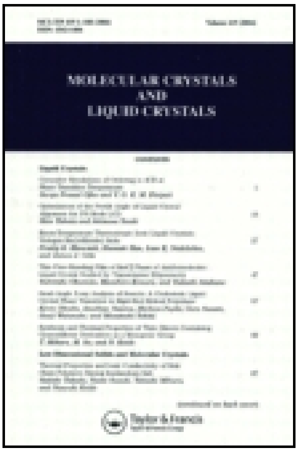

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Spectroscopy and Mechanism in Triboluminescence

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SPECTROSCOPY AND MECHANISM IN TRIBOLUMINESCENCE

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Abstract The presence of $\underline{C}^3\pi_u$ -> $\underline{B}^3\pi_g$ emissions of dinitrogen and photoluminescence in triboluminescence spectra provides information about the mechanism of light production.

Keywords: triboluminescence, fractoluminescence, photoluminescence emission and excitation, static electricity, dielectric breakdown, electrical discharge in air

The ability of some solids to emit light when they are fractured, otherwise known as tribo- or fractoluminescence, has been recognized for hundreds of years[1], probably even in pre-history. In the 1920's it was determined that sucrose and several other non-photoluminescent materials emitted a spectrum indistinguishable from the $\underline{C}^3\pi_u$ -> $\underline{B}^3\pi_g$ (second positive group) emissions of dinitrogen produced by an electrical discharge through air[2]; these emissions, reproduced in Figure 1 will be called "lightning" throughout this paper. The emission of lightning, and the fact that non-centric materials are more likely to be triboluminescent than centric ones[3,4,5,6,7,8], established triboluminescence as an electrical phenomenon. The light is most likely produced during a discharge between fresh surfaces produced upon fracture of the material.

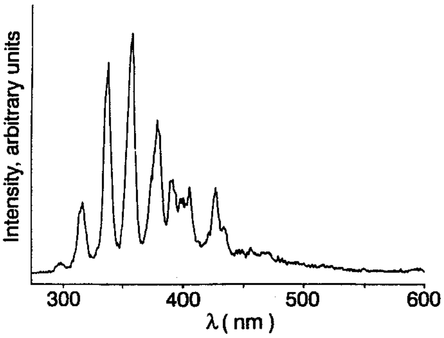

FIGURE 1 Triboluminescence spectrum of sucrose, 30 sec, 100 μ slit (4 pixel or 2.4 nm resolution), aluminum rod; a glass rod gives the same spectrum.

The triboluminescence spectrum of photoluminescent mate-

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[a] Linda M. Sweeting is a Professor and the other authors were undergraduate students at Towson State University during this research. Please address inquiries to Dr. Sweeting.

rials usually gives no such clear record of the origin of the excitation. For example, triethylammonium tetrakis(dibenzoylmethanato)europate[9,10] and nicotinium salicylate[11] (Figure 2), both of which produce emissions bright enough to be seen at the back of a dark lecture hall, have triboluminescence spectra nearly the same as their photoluminescence spectra, with no traces of lightning. Triboluminescence emissions very similar to photoluminescence will be called "tribophotoluminescence". In this paper we will give some examples of triboluminescence spectra and discuss the mechanistic implications.

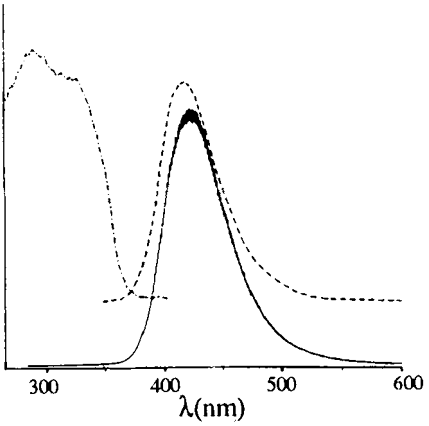

FIGURE 2 Photoluminescence (excitation _._. and emission - -) and triboluminescence - spectra of nicotinium salicylate (30 sec, 100 μ slit, glass rod).

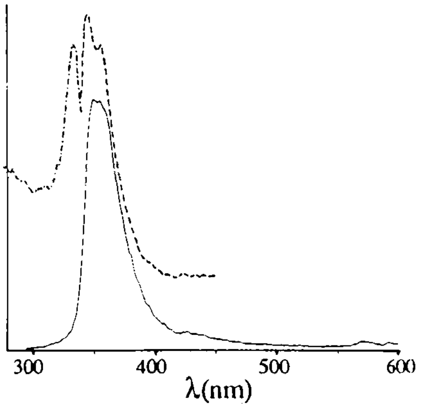

FIGURE 3 Photoluminescence (excitation _._. and emission - -) and triboluminescence spectra of acenaphthene (60 sec, 25 μ slit, glass rod).

A few materials, such as doped zinc sulfides[12,13], clearly produce their triboluminescence upon pressure-induced combination of defects and luminescent centers formed by irradiation and doping. However, most materials emit light only on fracture; several experiments have shown that the pressure at the time and place of emission is that of the surrounding atmosphere[14,15] and single crystal experiments show fracture immediately precedes light emission (by milliseconds)[16,17]. It has been claimed that acenaphthene emits light upon piezomodulation, without cracking, excited by the oscillating electric field produced by their own piezoelectricity[18,19]. The light emission, however, is erratic during this oscillation, suggesting cracking. Its triboluminescence spectrum, Figure 3, provides no clue about whether fracture occurs, but we have found that its triboluminescence disappears completely under liquids, suggesting that air may be necessary to its activity.

It has been proposed many times that the mechanism of triboluminescence of photoluminescent materials is similar to that of sucrose, namely that the primary event is charge separation upon fracture followed by a discharge which excites visible luminescence. Longchambon[20] believed that dinitrogen was excited by electron bombardment and that its UV-vis emission excited the photoluminescence of the solid. Indeed the uranyl nitrate hexahydrate he studied shows evidence of this indirect excitation of the uranyl photoluminescence. Figure 4 reveals that the triboluminescence of uranyl nitrate contains about 0.5% of lightning with the uranyl tribophotoluminescence. The relative intensities of the lightning lines are as significant than their presence: emissions below 350 nm (and above 380 nm) have been significantly reduced. The lightning appears to have been absorbed by the uranyl ion, suggesting that this absorption may be responsible for the excitation of the uranyl ion. We first noticed this selective absorption of lightning lines in our study of wintergreen candy[21]. Other spectral characteristics show that the crystals do absorb part of the triboluminescence emission. The tribophotoluminescence spectra of nicotinium salicylate (Figure 2) and acenaphthene (Figure 3) both show the typical depletion of the shortest wavelengths of the tribophotoluminescence in the region where the excitation (absorption) overlaps the emission. Such self-absorption is not surprising because the tribophotoluminescence comes primarily from cracks below the surface, but the photoluminescence is measured by surface excitation UV-vis light.

Encouraged by these results we decided to look for lightning in the spectra of other photoluminescent materials which are triboluminescent. We concentrated on materials whose photoluminescence is weak or at short wavelength and which might therefore allow more of the lightning to escape absorption. Several examples in the literature, such as cholesterol[6], showed exactly what we were looking for. We surprised at the diversity of spectral characteristics our study revealed.

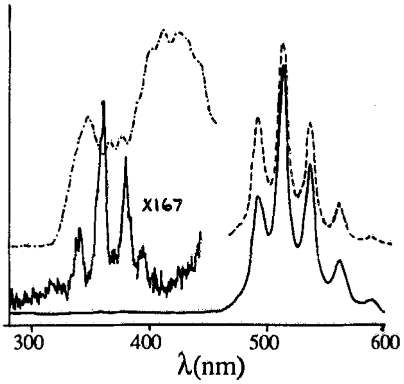

FIGURE 4 Photoluminescence (excitation _._. and emission - -) and triboluminescence spectra of uranyl nitrate hexahydrate (180 sec, 100 μ slit, glass rod).

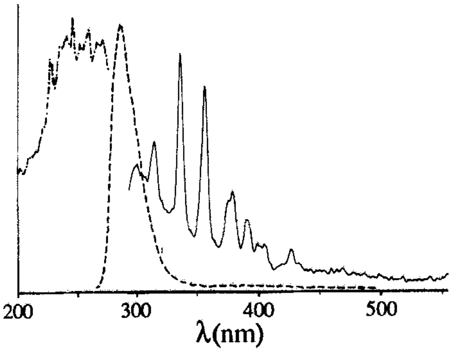

FIGURE 5 Photoluminescence (excitation _._. and emission - -) and triboluminescence spectra of sulfanilic acid (60 sec, 100 μ slit, glass rod).

The triboluminescence of sulfanilic acid (Figure 5) is typical of triboluminescence spectra observed for solids whose photoluminescence emission maximum is less than about 350 nm:

lightning superimposed upon a background of tribophotoluminescence. The lightning beyond 300 nm cannot be absorbed by this sample and its presence clearly reveals the presence of an electrical discharge through air during the triboluminescence. The simultaneous presence of both lightning and tribophotoluminescence allows but does not require that the tribophotoluminescence be excited by the lightning. The dinitrogen and the sulfanilic acid could be independently excited by electron bombardment, or a static discharge to the container might have produced the lightning. A static discharge cannot be called triboluminescence. To show that lightning absorption occurs, a material which absorbs light at wavelengths greater than 300 nm must be examined. The spectrum of weakly photoluminescent cinchonine (Figure 6) clearly shows lightning superimposed upon the weak tribophotoluminescence emission, with the intensities of the lightning lines much depleted in the region below 350 nm corresponding to the photoluminescence excitation of cinchonidine.

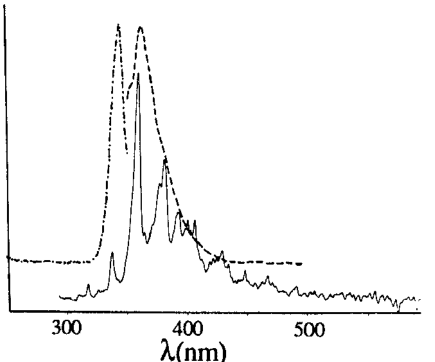

FIGURE 6 Photoluminescence (excitation _._. and emission - -) and triboluminescence spectra of cinchonine (30 sec, 100 μ slit, glass rod).

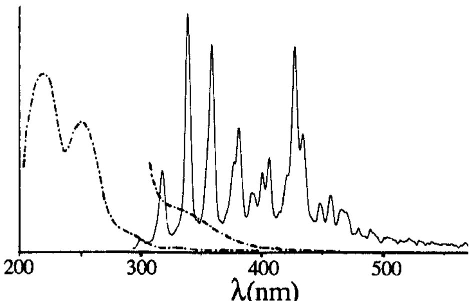

FIGURE 7 Triboluminescence spectrum of m-nitrobenzonitrile (30 sec, 100 μ slit). Ultraviolet absorption spectrum _._. in methanol solution; the expansion beyond 350 nm was obtained on a more concentrated sample.

m-Nitrobenzonitrile is not photoluminescent but its triboluminescence spectrum is unlike any in the literature or our experience. Figure 7 shows that its triboluminescence emission consists lines corresponding to lightning but with very different intensities; most dramatic is the fact that the weak emission at 427 nm is comparable in intensity to the bands that are normally the most intense (338 and 358 nm). We can detect no photoluminescence at 427 nm or elsewhere in UV-vis. We propose that the m-nitrobenzonitrile crystals absorb the lightning that is produced by its triboluminescence without being excited to tribophotoluminescence. We were unable to obtain an absorption spectrum of the solid, but the solution spectrum indicates that our proposal is correct - absorption occurs below about 425 nm, increasing at shorter wavelength.

We varied the force and implement with which we ground the sample and found that the relative intensities of the lines below and above 420 nm varied. Perhaps harder grinding permits more of the triboluminescence emissions to escape, or produces more lightning which overcomes the capacity of the solid to absorb - or perhaps the hard grinding causes an unrelated static discharge.

The triboluminescence spectrum of coumarin has been reported several times[22, 23, 24], with differences between the spectra much greater than could be accounted for by differences in resolution. Upon repeating this spectrum (Figure 8), we found that some of the differences could be ascribed to the variable presence of lightning in the triboluminescence spectrum along with tribophotoluminescence. In fact, the relative amount of lightning varied with the grinding implement and with force. Moreover, the relative intensities of the lightning lines are indistinguishable from the relative intensities observed for sucrose, even though coumarin's photoluminescence excitation overlaps the lightning emission. It was clear that the lightning and the photoluminescence in this case were independent events. We have concluded that the lightning observed in the spectrum of coumarin is from the discharge of static electricity, generated by rubbing the sample between rod and tube[25]. It is worth noting that these spectra were collected in mid-winter, when the indoor relative humidity was very low, and the literature spectra were obtained in Southern California[23]. To our knowledge, triboluminescence and static discharge have never before been identified in the same emission. We observed similar patterns of behavior for other materials. The literature contains several examples of unmodified lightning with tribophotoluminescence which we believe is also generated by coincidental static discharge.[26, 27]

It is much more difficult to detect lightning in the triboluminescence spectra of strongly photoluminescence materials. We previously examined the spectra of 9-anthracenecarbinols[8] and detected no lightning; with improved sensitivity we have detected traces of lightning in their spectra as well. 9-anthracenemethanol will illustrate. In an attempt to increase the signal-to-noise, we ground several samples in a row with the same rod; the lightning observed decreased as the rod was used (Figure 9) from 0.5% of the photoluminescence to less than the noise. Since the relative intensities of the lightning lines are indistinguishable from those of sucrose triboluminescence, we conclude that static charging has again occurred, with the intensity decreasing because the coated rod is not as hard. On another occasion, however, we did observe traces of lightning with highly modified intensities, about 0.07% of the photoluminescence (Figure 9d). We have observed traces of modified and unmodified lightning in several other strongly photoluminescent materials.

We conclude that there is significant evidence that the lightning produced by a electrical discharge through the surrounding atmosphere is frequently part of the triboluminescence of photoluminescent materials. Sometimes that lightning is just a static discharge, probably to the rod or container;

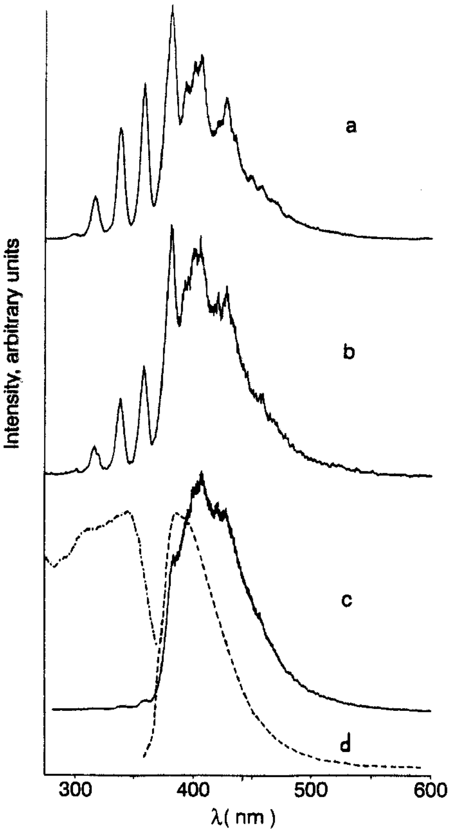

FIGURE 8 Triboluminescence spectra of coumarin (each 30 sec, 100 μ slit) using different grinding conditions, 30 sec each: (a) fresh glass rod, forcefully, Jan 1991; (b) fresh aluminum rod, forcefully, Jan 1991; (c) fresh aluminum rod, gently, Jan 1991; (d) photoluminescence spectrum of coumarin (excitation _._. and emission - -).

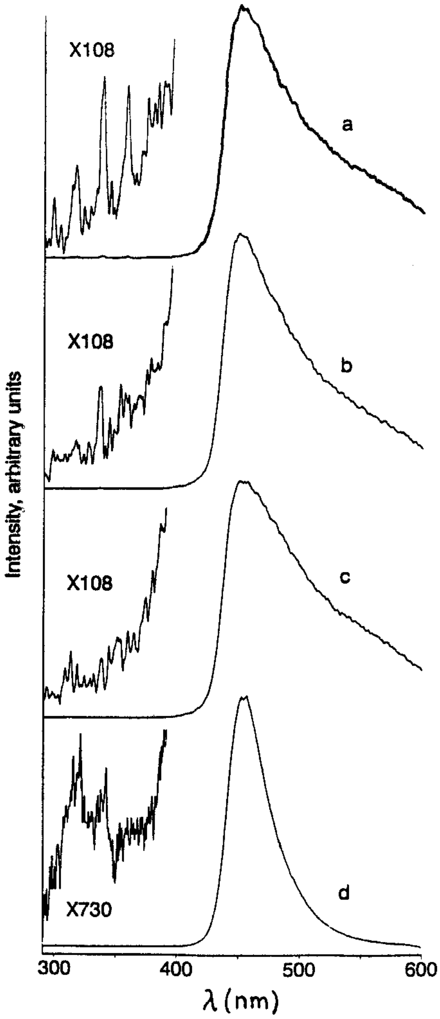

FIGURE 9 Triboluminescence spectra of 9-anthracenemethanol (100 μ slit), grinding forcefully with different rods on different days: (a) fresh aluminum rod, 60 sec, Jan 1990; (b) same aluminum rod and fresh sample, 60 sec, Jan 1990; (c) same aluminum rod and second fresh sample, 60 sec, Jan 1990; (d) glass rod, 480 sec, Sep 1988.

since the static discharge is concentrated on the surface of the material, the relative intensities of the lines show little or no sign of absorption by the sample. Where selective absorption of the lightning lines is observed, it is reasonable to conclude that at least part of the emission is actually part of the triboluminescence phenomenon, occurring within the crystals as they fracture. Absorption of the lightning suggests that the UV-vis emission of dinitrogen is the source of the photoluminescence excitation; however, simultaneous excitation of dinitrogen and the molecules of the solid by electron bombardment cannot be ruled out. We are continuing spectroscopic and other approaches to resolve this mechanistic uncertainty.

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[b] All spectra were obtained on EG&G PAR 1234 spectrometer, 1420 UV-sensitive diode array detectors cooled to the lowest possible temperature or -30°C, with 1460 OMA3 multichannel analyzers using a 100 micron slit (resolution 2.4 nm). Samples were ground in a pyrex test tube with either an aluminum or glass rod. No correction was made for detector and spectrometer characteristics but a sucrose reference spectrum was taken with each apparatus; differences were small.

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