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Triboluminescence with and without Air

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Twenty-three triboluminescent organic and inorganic materials were examined for crystal symmetry, differences between photoluminescence and triboluminescence emission spectra, spectroscopic evidence of an electrical discharge, and persistence of activity under liquids; some were also tested under other atmospheres. These experiments indicate that 18 materials were excited by a discharge, by either electron bombardment of the material or secondary excitation by the UV emissions of the surrounding gas. Five are apparently excited without a discharge, probably by the defect recombination characteristic of deformation luminescence.

Introduction

Triboluminescence, the emission of light by solids when they are stressed or fractured, is a very common phenomenon. According to literature estimates, 36% of inorganics, 19% of organics,[1] 37% of aromatic compounds, 70% of alkaloids,[2] and perhaps 50% of all crystalline materials[3] are triboluminescent. Moreover, this property can be useful in the study of wear[4] and material failure.[5−8] Photochemistry resulting from triboluminescence might contribute to the tribological degradation of materials and is implicated in the mechanism of explosions.[9] Despite its ubiquity and importance, triboluminescence is not well understood.

Triboluminescence has been examined spectroscopically and crystallographically for over 75 years.[10] Longchambon[2,10,11] observed that the triboluminescence emission spectra of sucrose, tartaric acid, cadmium sulfate, uranyl nitrate, and fluorite contained the line spectrum characteristic of an electrical discharge through air (almost exclusively the $^3\pi_u \rightarrow {}^3\pi_g$ bands, or second positive group, of N_2 characteristic of lightning). The nature of the emission was subsequently confirmed by others and is shown in Figure 1.[12−16] Longchambon also observed fluorescence or a continuum accompanying the N_2 lines for a few samples.[10] Early experiments indicated that the phenomenon was most commonly observed in noncentrosymmetric (noncentric), and therefore piezoelectric, materials and was absent in conductors,[17] confirming that charge separation is necessary for its observation. Longchambon was convinced that the process of light emission is as follows: separation of charge during strain and fracture to generate an electric field; dielectric breakdown of the surrounding air in that field; excitation of the N_2 molecules by electron bombardment; photoluminescence emission by the N_2; and, where possible, absorption of the N_2 UV−vis emission to stimulate fluorescence of the crystal. He also recognized that some materials, e.g., quartz, emitted light at least in part because they became hot.

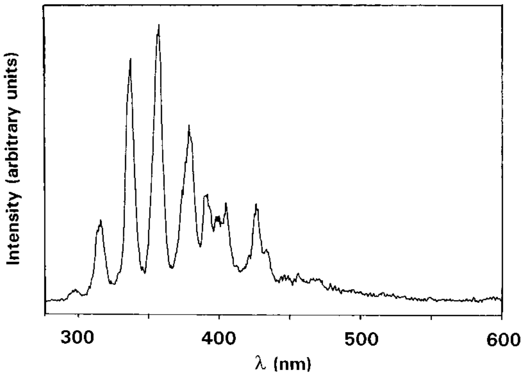

Figure 1. Triboluminescence spectrum of **1**, sucrose.

Triboluminescence, also known as mechanoluminescence, piezoluminescence, or fractoluminescence (part of fracto-emission), has subsequently been discovered in a wide variety of materials, many of which fail to exhibit the properties required for Longchambon's model. Several groups correlated triboluminescence with the lack of centrosymmetry needed for piezoelectricity but found that triboluminescent sulfates were only 53%

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noncentric,[18] nitrates and halogenates 50%,[19,20] aromatic organic compounds 68%,[21,22] and triclinic crystals 73%.[23,24] A wide variety of achiral polymers are also triboluminescent.[25−28] Even metals emit some light when fractured.[29]

Only triboluminescent materials that are not photoluminescent emit the N_2 spectrum—lightning—with certainty. There is little dispute that their triboluminescence emission is caused by an electrical discharge. Dickinson et al. clearly demonstrated discharge upon failure for filled and unfilled polymers,[28] single-crystal MgO,[30] sugar,[31] and various interfaces[25,32] by detecting light, radio signals, electrons, and ions at the moment of fracture under vacuum.[33]

In contrast, most photoluminescent materials[17] and minerals[34] that are triboluminescent emit their photoluminescence when fractured; we will call this emission tribophotoluminescence. Materials with strong photoluminescence at wavelengths greater than about 420 nm show little or no trace of N_2 lines in their triboluminescence; many that do, such as uranyl nitrate, present the relatively weak N_2 lines with altered intensities consistent with absorption by the material.[16] N_2 lines might be produced in all cases but might be absorbed so efficiently by the materials that none are seen in the spectrum.

Although Longchambon's mechanism accounts for most of the observations, many photoluminescent materials exhibit surprising properties such as emission under liquids,[35] emission under gases other than air,[17,35−38] and tribophotoluminescence spectra different from their photoluminescence spectra.[39] Doped zinc sulfides (phosphors) give spectra identical to their electroluminescence spectra, not their photoluminescence spectra, and do not require fracture for emission.[40] Instead, they emit light on deformation,[41] which is characteristic of their defects, as do impure magnesia[6] and X-irradiated alkali halides.[40,42] Heat or a single strain cycle can destroy their triboluminescence.[43−45] These observations suggest that their triboluminescence, electroluminescence, and thermoluminescence occur by the same process, i.e., migration of defects and light emission upon recombination of electrons with positive sites.[17,46] Interestingly, pure alkali halides emit only on fracture and, like quartz,[47] produce the N_2 spectrum and a continuum that can be ascribed to blackbody radiation.[38]

We attempt in this paper to distinguish the major possibilities for excitation of triboluminescence: discharge that excites the surrounding gas by electron bombardment, producing photoexcitation of the material by the UV emissions of the gas; discharge that directly excites the material by electron bombardment; and a deformation mechanism that does not require fracture. We take the simple approach of examining the triboluminescence of 23 materials, more than half photoluminescent in the visible region. Their triboluminescence spectra are examined for N_2 lines and differences from their photoluminescence spectra, their crystal structures for symmetry, and their triboluminescence intensities for persistence under liquids. Representative materials are also recrystallized under atmospheres other than air. We find a broad range of behavior under these conditions. We consider in detail the processes by which liquids and other atmospheres could affect the triboluminescence and draw conclusions about the mechanism(s) of triboluminescence.

Experimental Section

a. Materials. The compounds used are listed in Table 1. Their sources are as follows: **1**−**4**, **10**, **13**, **18**, and **20** from Aldrich Chemical; **5**, **6**, **9**, **14**, and **15** from Fisher Chemical; **8**, **11**, and **12** from Eastman; **7** from J. T. Baker; and **17** from Johnson-Mathey. **21**, also known as salicyl salicylate or salsalate, was provided by 3M. **16**,[48] **19**,[49] **22**,[35,50] and **23**[51] were synthesized according to literature methods and purified by one or two recrystallizations; each had spectroscopic properties and melting points acceptably close to literature values. Unless otherwise stated, commercial samples were used as received, including a sample of **19** from Aldrich with a pink color that was used for the examination during recrystallization.

b. Methods. Crystallographic data are from the literature and were located using the Cambridge Structural Database;[52] the original sources are reported in Table 1. Two forms of **23** were reported by Weitz;[51] we were able to grow only the

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Table 1. Crystallographic and Spectroscopic Properties of Triboluminescent Materials

A. No Emission under Liquids

				spectroscopic properties			
ID	compound	space group/ SHG[a]	triboluminescence intensity[b] in air	% lightning[c] in triboluminescence	triboluminescence emission maximum,[d] nm	photoluminescence emission maximum, nm	photoluminescence excitation maximum, nm
1	sucrose	$P2_1$[71]	3	100[11]	337 (N_2)	NA	NA
2	3-nitrobenzonitrile	SHG +	3	100[72]	358 (N_2)	NA	NA
3	(+)-cinchonine	$P2_1$[73]	3	>86[16]	358 (N_2)	362	340
4	triphenylphosphine oxide	$P2_1/c$[74] SHG −	3	70[63]	358 (N_2)	384	335
5	sulfanilic acid monohydrate	$P2_1/c$[75] SHG +	3	62−78[16]	337 (N_2)	287	259
6	potassium hydrogen phthalate	$Pca2_1$[76]	3	42	337 (N_2)	319	230
7	triphenylmethane	$P2_12_12_1$[77]	3	14−28[63]	425 (N_2)	401	241, 392
8	isopropyl phenyl carbamate	$Pca2_1$[78]	3	20[72]	315[e]	302	259
9	resorcinol	$Pna2_1$[79]	4	10[72,80]	309[e]	299	282
10	1,10-phenanthroline	$C2$[81]	4	3−12	446	443	364
11	anthranilic acid	$P2_1cn$[82]	3	<6[61]	430	425	280
12	acenaphthene	$Pcm2_1$[83]	4	<0.1[16,80]	355	346	333

B. Some Emission under Liquids

				spectroscopic properties			
ID	compound	space group/ SHG[a]	triboluminescence intensity[b] in air	% lightning[c] in triboluminescence	triboluminescence emission maximum,[d] nm	photoluminescence emission maximum, nm	photoluminescence excitation maximum, nm
13	coumarin	$Pca2_1$[84]	4	3−50[16,72,80,85]	382 (N_2)	394	241, 346
14	4-anisidine	$Pca2_1$[86]	3	<0.5−4.5[72,80]	359	357	272
15	uranyl nitrate hexahydrate	$Ccm2_1$[87]	4	0.5[10,16,88]	508	508	402
16	9-anthracenemethanol	Cc[48]	4	<0.39−0.9[48,72]	452	447	411
17	hexaaquodichloroterbium chloride	$P2/n$[58] SHG −	5	<7	543	544	377
18	3-aminophenol	$Pca2_1$[89]	5	<2[80]	330	322	259
19	*N*-acetylanthranilic acid	$Fdd2$[90]	5	<0.4[80]	522	520	362
20	9,10-dihydroanthracene	$P2_1$[91]	5	<0.4	410	409	385
21	2-carboxyphenyl 2-hydroxybenzoate	$Fdd2$[92,93]	6	<0.3[92]	456	450	334
22	triethylammonium tetrakis(dibenzoyl-methanato)europate	$I2/a$[50] SHG +	6	<0.2[50,56,80]	612	612	398
23	nicotinium salicylate	$P2_1$[53]	6	<0.1[16]	423	414	325

[a] **2** and centric crystals were tested for second-harmonic generation (SHG) with a Nd:YAG laser. [b] Compared to sucrose (**1**), intensity = 3, and europate **22**, intensity = 6. [c] Percentages are based on peak height. Percentages labeled $<X$ are noise levels if no lightning was observed. Percentages labeled $>Y$ are estimates for spectra in which there was an underlying broad emission. Where a range is given, the relative intensity of the lightning varied from spectrum to spectrum. [d] (N_2) indicates that a dinitrogen emission line provided the intensity maximum. [e] Absorption of the triboluminescence by the glass container created a bathochromic shift.

triboluminescent one, whose crystal structure was identical to that in the literature.[53,54] We were unsuccessful at growing crystals of **2** suitable for crystallography; this compound was determined to be noncentrosymmetric by (green) second-harmonic generation (SHG) when irradiated with a (red) Nd:YAG laser.[55] All materials found to be centric by crystallography were also tested for SHG.

Triboluminescence spectra were obtained as previously described using an EG&G PARC OMA III optical multichannel analyzer, model 1234 spectrometer, and model 1421HQ intensified diode array detector with Pelletier cooling.[56,57] The resolution is estimated to be 1.2 nm.[56] The wavelength uncertainty for tribophotoluminescence is higher than the estimated resolution because of the difficulty of determining the maximum for a broad, noisy peak. If the characteristic line spectrum of N_2 was observed in the triboluminescence, the height of the most intense line above any underlying emission (not always the 0,0 transition at 337 nm because of absorption) was compared to the height of any tribophotoluminescence to determine the approximate percentage of N_2 lines reported in Table 1. This method overestimates the relative intensity of N_2 lines (except for 100%) because its emissions are much narrower than those of the tribophotoluminescence. References are given in Table 1 to literature spectra. All numerical data and calculations were generated from our spectra. If no N_2 lines were observed, the upper limit of N_2 intensity (Table 1) was estimated to be less than the peak-to-peak maximum noise. **17** was not examined at less than 400 nm;[58] the noise at the position of the N_2 lines at 430 nm, corrected for the ratio of the heights of the emissions at 337 and 430 nm, provided an upper limit for that compound. N_2 lines in **17** are expected to be faint, like those in other metal-centered tribophotoluminescence (**15** and **22**).[50,56] In those cases where the photoluminescence maximum was less than 320 nm (**5**, **8**, and **9**), the apparent tribophotoluminescence maximum just above 300 nm created by glass absorption was used; such an approach results in an even higher estimate of the percent of N_2 lines in the spectrum.

Photoluminescence spectra were obtained for the solid materials on a Perkin-Elmer LS-50 instrument with 2.5-nm resolution. Thus, wavelength differences between photoluminescence and triboluminescence maxima of less than 4 nm are not significant. The excitation wavelength selected was the one >200 nm that gave the most intense emission; we found no differences among emission spectra excited at different wavelengths for these materials other than total intensity. We report the wavelength of the most intense band in Table 1.

The relative triboluminescence intensities in Tables 1 and 2 were evaluated by crushing small samples (50−100 mg) against the bottom or side of a test tube with a glass rod. Because the human eye was the detector, materials with no fluorescence above about 400 nm (**1**−**3**, **5**, **6**, **8**, and **9**) would not be recognized to exhibit triboluminescence unless N_2 lines, which extend beyond 500 nm,[59] were emitted. The intensity scale represents differences in intensity that can be distinguished when the eye is dark-adapted for at least 15 min. The standards are barely visible =1, sucrose (**1**) = 3, and triethylammonium tetrakis(dibenzoylmethanato)europate (**22**) = 6, as previously described.[57] Intensity ratings are reproducible to 1 unit. A comparison with the quantitative data of Beese and Zink[60,61] suggests that the relative intensity values in Tables 1 and 2 correspond to orders of magnitude in light intensity. The relative intensities observed with an UV-sensitive PM tube would be higher for materials whose emissions are predominantly UV.

We attempted examinations under other atmospheres by recrystallization of **1** (water, methanol, ethanol), **5** (water), **12** (ethanol), **13** (cyclohexane, water), **16** (ethanol), **17** (aqueous HCl), and **22** (methanol). The gases used are reported in Table 2. **1**, **5**, and **13** were chosen because their spectra exhibited emission from N_2. **16**, **17**, and **22** were chosen because there was little or no evidence of N_2 lines with their tribophotoluminescence. **12** was chosen because of reports that its tribophotoluminescence does not require cracking.[62] Samples were placed in a three-necked flask with an appropriate volume of the recrystallization solvent, with one neck attached to a Schlenk line and the others to septa. A glass rod was inserted through one septum to permit grinding of the sample without opening of the container. Each sample was submitted to five freeze−pump−repressurize−thaw−warm-to-dissolve−cool−crystallize cycles. The solvent was removed from the crystals with a cannula into a second flask under reduced pressure of the same gas. When the crystals appeared dry, the cannula was removed; the flask was isolated from the line with a stopcock and removed to a darkroom for examination. We tried sulfur hexafluoride, used to prevent dielectric breakdown in high-voltage equipment, but the pump cycle took too long. Thus, we continued with the gases that others had used, including carbon dioxide,[17,63,64] helium,[58,65,66] and argon.[38,67−69] We did not use neon because of its high cost. Unfortunately, we were unable to examine **1** because we could not accomplish the crystallization step, but previous workers have done so.[17]

To examine the triboluminescence under liquids, two samples of each compound were first crushed in air.[56] Care was taken not to pulverize the samples completely as the intensity decreases with crystal size.[70] Then, 1−2 mL of either 2-propanol or hexane was added to each tube, and the sample was crushed and evaluated again. In some cases, the triboluminescence was not quenched until the material had been stirred and crushed a few times. We recorded the behavior under the liquid both during and after this brief period, when the intensity seemed to have stabilized. The samples were examined afterward. If crystals still remained, the intensity reported in Table 2 is that after stabilization. If the materials had dissolved (**10**, **14**−**16**), their emissions are reported during dissolution. At least two persons evaluated each sample (a genuinely double-blind experiment as total darkness was required), and most tests were done at least twice.

To reduce the concentration of air around the crystals still further, the triboluminescence of most materials was further tested by recrystallizing them from warm 2-propanol and/or hexane (or methanol or toluene when that was impossible) and examining the triboluminescence of any crystals that grew before they were exposed to air. In most cases, some evaporation of the solution was necessary for significant crystallization. If the materials crystallized above the solution, their activity is not reported. After examination, the samples were evaporated to dryness at room temperature and reexamined for triboluminescence activity.

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Table 2. Triboluminescence Activity in Air and under Other Atmospheres and Liquids, "Without" Air

A. No Emission under Liquids

		triboluminescence intensity[a]							
ID	compound	in air	in other gas	gas	under 2-propanol	under hexane	in mother liquor	recrystallization solvent	after drying in air
1	sucrose	3	Y	Ne[36]	0[b]	0			
			Y	Ar[67]					
2	3-nitrobenzonitrile	3			0	0	0	2-propanol	0
3	(+)-cinchonine	3			0	0	0	2-propanol	2
4	triphenylphosphine oxide	3			0	0	0	2-propanol	0
5	sulfanilic acid monohydrate	3	0	He	0	0			
6	potassium hydrogen phthalate	3			0	0			
7	triphenylmethane	3	Y	CO_2[63]	0	0	0	2-propanol	1
8	isopropyl phenyl carbamate	3			0	0			
9	resorcinol	4	Y	Ar[94]	0	0			
10	1,10-phenanthroline	4			0[c]	0	0	2-propanol	4
11	anthranilic acid	3			0	0	0	2-propanol	1
12	acenaphthene	4	4	He	0[b]	0	0	2-propanol	6
			Y	Ar[94]					

B. Some Emission under Liquids

		triboluminescence intensity[a]							
ID	compound	in air	in other gas	gas	under 2-propanol	under hexane	in mother liquor	recrystallization solvent	after drying in air
13	coumarin	4	4	He	3	3	0	2-propanol	5
			Y	Ar[94]			0	hexane	4
14	4-anisidine	3			3[c]	3	0	hexane	0
15	uranyl nitrate hexahydrate	4	Y	Ne[36]	4[b,c]	4	0	2-propanol	0
16	9-anthracenemethanol	4	3	He	2[d]	2[d]	4	2-propanol	5
			4	Ar					
			4	CO_2					
17	hexaaquodichloroterbium chloride	5	5	He	2	0			
18	3-aminophenol	5	Y	Ar[94]	4	2	0	toluene	4
19	*N*-acetylanthranilic acid	5			3[b]	3	5	2-propanol	5
20	9,10-dihydroanthracene	5			3[b]	0	0	2-propanol	5
21	2-carboxyphenyl 2-hydroxybenzoate	6			4	4	5	2-propanol	6
							6	toluene	6
22	triethylammonium tetrakis(dibenzoyl-methanato)europate	6	6	He	2	2	5	methanol	6
			6	Ar		Y[e]			
			4	SF_6					
			Y[35]	undefined					
23	nicotinium salicylate	6			5	4	4	toluene	6

[a] Compared to sucrose (**1**), intensity = 3, and europate **22**, intensity = 6; Y = "yes, others observed emission." [b] Results are the same under methanol. [c] Sample dissolved; observations are reported during dissolution. [d] Most of the sample dissolved. [e] Under 2-methylpentane.[35]

Results

a. Selection of Materials. The identities of **1**−**23**, the space groups of their crystals, and the spectroscopic properties of their triboluminescence and solid-state photoluminescence emissions are presented in Table 1, along with references to literature reports. Table 1A contains those materials whose triboluminescence disappears under added liquids, and Table 1B includes those whose triboluminescence persists under added liquids. In both sections of the table, materials are placed in order of decreasing percentages of N_2 lines in the spectrum; those for which N_2 lines were actually observed are placed before those for which a maximum was set from the noise level.

b. Crystal Symmetry. Noncentric crystals dominate this group: only **4**, **5**, **17**, and **22** were found to be centric by crystallography (Table 1). Because crystallography cannot always detect deviations from centrosymmetry,[95] the centric materials were examined for second-harmonic generation (SHG) with a Nd:YAG laser;[55] the presence of SHG shows that **5** and **22** are, in fact, noncentric.[7] **11** has three crystal forms,[61] and **23** has two crystal forms,[51] with only the noncentric form being triboluminescent in each case. **9** might also have multiple crystal forms.[52,79] Thus, of the 23 materials, only **4** and **17** were clearly centric.

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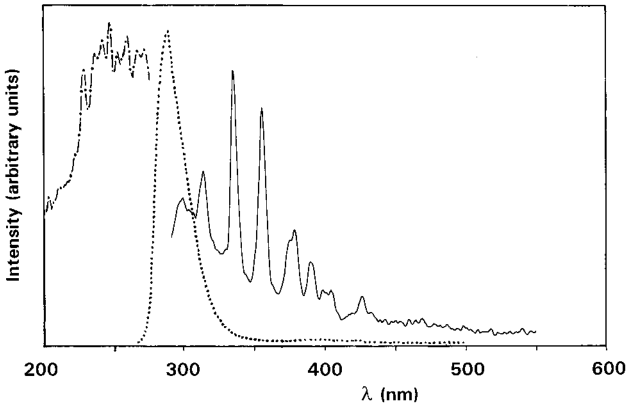

Figure 2. Sulfanilic acid monohydrate, **5**: triboluminescence emission (—), and photoluminescence emission (• • •), and excitation (— • — •) spectra.

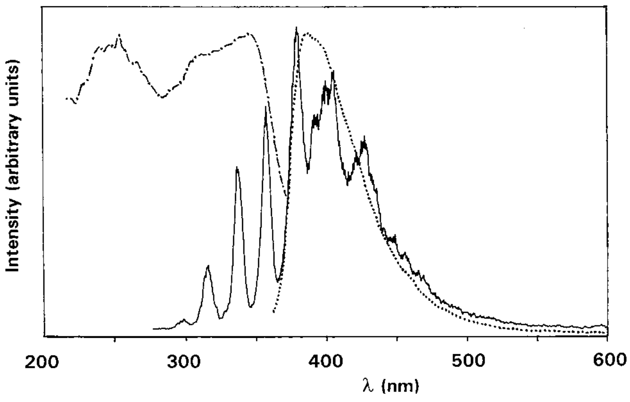

Figure 3. Coumarin, **13**: triboluminescence emission (—), and photoluminescence emission (• • •), and excitation (— • — •) spectra.

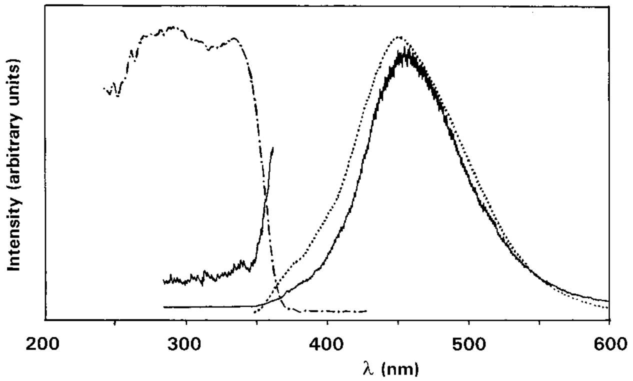

Figure 4. 2-Carboxyphenyl 2-hydroxybenzoate (salicyl salicylic acid), **21**: triboluminescence emission (—), and photoluminescence emission (• • •), and excitation (— • — •) spectra. The triboluminescence intensity from 280 to 360 nm is also shown expanded by a factor of 20.

We found that both the triboluminescence and the photoluminescence of **17** faded with time, an observation that we intend to investigate further. Temporary triboluminescence like that exhibited by **17** has been observed in arsenolite (As_2O_3) and has been ascribed to relaxation of crystal defects on standing.[96,97] In the case of **17**, a change in hydration is also possible.

c. Triboluminescence and Photoluminescence Spectra. The triboluminescence spectra of typical samples, namely, **1**, **5**, **13**, and **21**, are presented in Figures 1−4. Emission lines from a discharge through N_2 are plainly visible in the spectra of **1**, **5**, and **13** (Figures 1−3) and absent from that of **21** (Figure 4). Table 1 reports the wavelengths of the maxima for photoluminescence excitation and emission, the wavelength maximum for triboluminescence emission, an estimate of the percentage of the emission from N_2 lines, and references to the spectra that others have published. N_2 lines are readily and reproducibly observable in the spectra of **1**−**10**, **13**, and **15**; they are also frequently observed in the spectra of **14** and **16**. The lightning lines of **5**, **6**, **8**, **9**, and usually **16** have intensities indistinguishable from those of an air discharge.

The tribophotoluminescence maximum is at slightly longer wavelength than the photoluminescence maximum for **11**, **12**, **16**, **18**, **21**, and **23**. For **8** and **9**, the maximum is at significantly longer wavelength than the photoluminescence because of absorption by the glass container. For **1**−**7** and **13**, the maximum is a N_2 line. The tribophotoluminescence and photoluminescence spectra of **4**, **7**, and **20** were dominated by impurities; those of **7** and **20** suggested contamination by polynuclear aromatic compounds. Pure **4** has been shown not to be triboluminescent.[98] **4**, **7**, and **20** were retained in the study to determine whether triboluminescence activity from impurities is different in its response to surroundings from triboluminescence intrinsic to the material, as it is for doped zinc sulfides.[40,99]

d. Triboluminescence in Atmospheres Other than Air. Table 2, parts A and B, compares the triboluminescence activity of **1**−**23** "in air" with that when the materials are recrystallized under another atmosphere ("gas") in the column "in other gas".

We found that the triboluminescence activity of most of the compounds tested, i.e., **12**, **13**, **16**, **17**, and **22**, persisted under helium, carbon dioxide, argon, and sulfur hexafluoride with negligible change in intensity,

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but that of **5** disappeared under helium. **5** is the only material tested whose *visible* emission is entirely from N_2. The triboluminescence activity of **5** was partially restored by admitting air to the sample. We include in Table 2 the results of others, indicated by a Y for "yes, triboluminescence persists". Although these experiments are not thoroughly described, it appears that the air was pumped out and the new gas introduced *without* redissolving the sample; no information was given on the number of gas exchanges. The triboluminescence of **1** is red under neon, and that of **15** is red and green.[36]

e. Triboluminescence under Liquids. The columns labeled "under 2-propanol" and "under hexane" in Table 2 display the triboluminescence activity after these two liquids were poured onto solid samples. The triboluminescence of half of the materials (**1**−**12**, Table 2A) was completely extinguished under either 2-propanol or hexane; that of the remainder (**13**−**23**, Table 2B) was unaffected or only slightly affected. With the exception of **13**, all of the materials with a high percentage of N_2 lines in their spectra were quenched by addition of liquids.

f. Triboluminescence under Mother Liquor. The materials were further tested with minimal exposure to air while they were still immersed in their recrystallization solutions. The results are presented in Table 2 in the column labeled "in mother liquor", from the "recrystallization solvent". It was not always possible to use 2-propanol and/or hexane. In some cases, the solubility was too high (**8**, **9**, **14**, **18**), and in others it was too low (**1**, **5**, **6**, **22**); still others gave a syrup or produced crystals only on the walls above the solution (**18**, **23**). For **13**−**23** we substituted methanol or toluene when necessary. We examined the triboluminescence of both **13** and **21** under two mother liquors and found no significant difference in behavior. Only **16**, **19**, and **21**−**23** were triboluminescent in their mother liquors. We did not examine **1**−**23** for crystalloluminescence.

To ensure that the materials had not been changed by the recrystallizations, the solutions were evaporated to dryness and reexamined; the results are presented in the column "after drying in air" in Table 2. As expected, the activity of the hydrate **15** did not return, presumably because the material was changed; we assume hydrate **17** would behave similarly. Further recrystallizations of **15** and **17** were not attempted. Activity also failed to return for **2**, **4**, and **14** and barely returned for **3**, **7**, and **11**.

Discussion

a. Selection of Materials and Methods. Crystalline materials were selected for this study whose visible triboluminescence intensity was at least as great as that of sucrose to ensure that triboluminescence would be visible even if the experiments reduced its intensity (Table 1). The selection also ensured a range of spectroscopic properties, including some compounds whose emission spectra were predominantly the result of a discharge and some whose emission showed little or no evidence of a discharge; **12** was selected because other researchers had observed light emission from it without observing fracture.[62]

The gases selected had all been used previously to attempt to alter triboluminescence (see Table 2). Previous studies gave very little justification for the choice of gases, except for an implicit assumption that the emission spectrum would change if gas luminescence alone were responsible for the triboluminescence. Helium has been reported to quench[58] or significantly reduce triboluminescence,[66] but did not affect that of *N*-isopropylcarbazole.[100] Similarly, carbon dioxide sometimes[17] quenched it but not always.[63] Neon increased the intensity of triboluminescence,[37] argon reduced it[67] or left it unchanged,[94] and sulfur hexafluoride reduced it significantly.[38] In general, the smallest effect of atmosphere was observed with photoluminescent materials. These erratic results might represent real differences between solids and gases or simply differences in the effectiveness of gas exchange.

We believe that repeated *solution* freeze−pump−thaw cycles followed by crystallization is the most effective way to replace traces of air inside and around the crystals with an alternate atmosphere. With similar procedures, *cis*-4-octene gave red emissions under neon,[101] and **9**, **12**, **13**, and **18** gave the same emission under argon,[94] but the piperidinium salt of a europate like **22** gave no emissions under helium.[58]

The liquids chosen, 2-propanol and hexane, were selected to provide good wetting of the surface of these materials (low contact angle) and a range of dielectric constants, 8.3 and 1.9, respectively,[102] but low solubility. Water was not used because its failure to wet the mostly hydrophobic surfaces could result in air bubbles being trapped on the surfaces of the crystals; only **1**, **6**, **15**, and **17** are likely to be wetted, and dissolved, by water. Moreover, water's high dielectric constant and conductivity would make it difficult to compare the results with those from the other liquids. Other investigators have had varying degrees of success with water. Some found only a weakening effect,[17,103,104] and others found that water did quench triboluminescence.[37,49] Brady and Rowell found that fracture of granite under water produced lines from atomic and molecular hydrogen.[65] Both lightning emitters[12,105] and tribophotoluminescent solids[35,58,64] have been observed to emit less strongly under less polar liquids such as ether, ketones, and hydrocarbons.

We selected a visual comparative scale for simplicity, as large differences were expected. Finer distinctions in activity could be made, and weaker samples could be studied, with a broad-range PM tube and a mechanical grinder able to deliver the same force to each sample, but a PM tube would be unable to detect changes in color.

b. Crystal Symmetry and Triboluminescence. Noncentric materials are piezoelectric, separating charge across the material under strain. Fracture with a component perpendicular to the piezoelectric axis will separate faces with opposite charge. If the electric field across the gap is great enough, dielectric breakdown will occur, and electron bombardment will excite the mol-

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ecules of the vapor in the gap. According to the Longchambon mechanism,[10] the light emitted by the gas is then responsible for the triboluminescence seen and for the excitation of the material's photoluminescence. Most of the materials in Table 1 are noncentric and can separate charge under strain (**7** requires a torsional strain).

Crystallographically, **4**, **5**, **17**, and **22** are centric, but crystallography, with its default assumption of centrosymmetry, can miss some noncentric structures.[95] A positive SHG test clearly indicates that **5** and **22** are also noncentric.[55] Although a failure to observe SHG could have causes other than centrosymmetry,[106] it appears that **4** and **17** are centric. Thus, 91% of the materials studied are clearly noncentric and thus piezoelectric.

For materials that are crystallographically centric, impurities are often a source of triboluminescence activity.[57,61] **4** is a well-known material with several crystal forms, all centric. Hocking et al. found crude **4** to be triboluminescent;[98] the activity was lost after two recrystallizations from acetone, suggesting that impurities are the source of its triboluminescence. The colors or the photoluminescence spectra of noncentric **7**, **14**, and **20** indicate that they too are impure.

Disorder can also be a source of triboluminescence activity. Crystallographically, **22** has been found to be either centric and disordered[50] or noncentric;[58] SHG shows that it is noncentric. Although the crystal structure of centric **17**[58] reveals little disorder (just one water ligand), we found that the triboluminescence of this material disappeared after standing for several years. Such temporary triboluminescence has previously been associated with the relaxation of crystal disorder on standing.[96]

Local dissymmetry caused by impurities or disorder can be sufficient to support nonlinear optical effects such as SHG in crystallographically centric crystals.[107,108] If phase matching is not possible, the size of the symmetry defect would need to be less than the coherence length (a few micrometers), but if phase matching is possible, the defect could be larger.[106] SHG could be observed from dissymmetric regions comparable in dimension to the wavelength. Such defects could be responsible for the SHG of crystallographically centric **5** and **22**. Local polarity with characteristic lengths of 100 μm generates observable pyroelectric domains in centric inclusion compounds.[109] Similar polar defects caused by impurities or disorder could provide sufficient piezoelectric polarization to enable triboluminescence; the size of the defect necessary will depend on other properties of the solid.

It has also been pointed out that ionic materials such as sodium chloride can fracture along planes that separate charge.[110] Even if a small fraction of the fracture occurs along those planes, sufficient potential might be generated locally to initiate a discharge. Such charge separation could occur for ionic **17** and **22**.

The crystal symmetries of these materials are thus consistent with a mechanism that requires electrical polarization of the crystal, regardless of whether fracture is necessary. Mechanisms that involve defect recombination do not require noncentric crystals.

c. Triboluminescence Spectra. The triboluminescence emissions of **1**−**10** and **13**−**15** reliably have part of their visible emissions from lightning, as illustrated in Figures 1−3. **1** and **2** exhibit only a N_2 discharge spectrum (Figure 1), with the relative intensities of **2** altered by its broad absorption bands at 222 and 250 nm. To our knowledge, **2** is the only material to exhibit absorption of N_2 lines in its triboluminescence without also exhibiting photoluminescence.[16]

3, **4**, **7**, **10**, **13**, and **15** exhibit N_2 lines with two changes: the relative intensities of the N_2 lines are altered, and a broad emission corresponding to their photoluminescence accompanies the lines. The relative heights of the N_2 lines for **1** (Figure 1) at 337 and 358 nm are approximately equal, and that at 380 nm is about half, typical of a discharge in air at that resolution.[56,59] However, the lines produced by **13** (Figure 3) at 337, 358, and 380 nm are about equal in height, indicating that the N_2 lines at 337 and 358 nm have been partially absorbed by the solid. Published spectra for **3** and **15** show a similar pattern.[16] The absorption of N_2 lines is consistent with excitation of the photoluminescence of these materials by the UV emissions of N_2.

The triboluminescence spectra of **5**, **6**, **8**, and **9** also consist of ultraviolet photoluminescence with N_2 lines superimposed, as illustrated by the spectrum of **5** in Figure 2. The visible part of the spectrum consists almost entirely of N_2 lines with normal relative intensities. These materials might be unable to absorb any of the N_2 lines, as the shortest-wavelength $^3\pi_u \rightarrow {}^3\pi_g$ line is a weak one at 269 nm,[59] lower in energy than is needed to excite **5**, **6**, and **8**. The weak tribophotoluminescence of these materials is probably excited by electron bombardment rather than UV emissions of the N_2. Dickinson's examination of organic polymers and other materials[111−114] shows clearly that electron bombardment of the surface does occur during fracture and that some electrons have sufficient energy to excite the crystal or the gas.[115]

7, **10**, and **13**−**16** show varying amounts of lightning in their spectra, depending on the force and implements used;[72] the variation is particularly large with **13** (Figure 3).[72] Although the N_2 lines of **7**, **10**, and **13** have clearly been absorbed by the material, those of **14**−**16** are faint and noisy, making it difficult to be sure of their presence or relative intensities. When the N_2 lines of **15** are seen, their intensities indicate absorption. The absence of N_2 lines in some spectra might be a conse-

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quence of poor sensitivity, but those of **14** and **16** vary in intensity even when the sensitivity is similar. **16** received far more attention than the other samples because we selected it to search for traces of N_2 lines. Of 25 spectra, 11 showed N_2 emission lines; of those, 9 were definitely from an independent discharge as their relative intensities seemed normal. Thus, at least part of the production of lightning for **16** originates in a separate, parallel discharge between the sample and the glass container or rod.[72] It is unlikely that the discharge is between the implements, as scraping a test tube with a glass rod produces long-wavelength broadband emission like the blackbody emission seen by Chapman and Walton for glass.[47] The triboluminescence spectra of **14** and **16** are consistent with excitation either by absorption of the lightning lines or by electron bombardment. The spectrum of **21** in Figure 4 illustrates how difficult it is to prevent observer bias in detecting lightning lines: although there is a small bump at 338 nm and another at about 318 nm, which might be assigned to N_2, there is no line at 358 nm, beyond **21**'s intense absorption, and thus probably no lightning in this spectrum.

Nearly half of the materials in this study, *namely*, **11**, **12**, **17**−**23**, and usually **14**−**16**, provide no spectroscopic evidence of a discharge; Figure 4 shows the emission for **21**. Even if a discharge had occurred, the lines from excited N_2 would be absorbed quite efficiently by these materials, whose broad excitation at 330−380 nm is ideally matched to the N_2 lines. For example, the photoluminescence excitation maximum of **12** is at 333 nm, almost perfectly matched to the most intense line of the N_2 lines at 337 nm.[16] A comparison with wintergreen candy will illustrate the absorption efficiency. The candy is 0.5% fluorescent methyl salicylate (absorption maximum at about 300 nm), and 50% of its triboluminescence intensity is from N_2 lines.[116,117] Assuming that doubling the concentration of the photoluminescent material results in absorption of twice as much lightning and emission of twice as much photoluminescence, a solid consisting of 90% photoluminescent material would have less than 0.3% of its triboluminescence from N_2, a level unlikely to be detected. When the triboluminescence emission is the photoluminescence of an impurity, as it probably is for **4**, **7**, and **20**, one might expect a spectrum like that of wintergreen candy, with a significant percentage of lightning lines; **4** and **7** do indeed exhibit lightning lines, but **20** does not. There are no other unusual spectral features in the impure materials.

Further evidence of efficient absorption is provided by the tribophotoluminescence spectra of **11**, **12**, **16**, **18**, **21**, and **23**. In these materials, the tribophotoluminescence is shifted to a wavelength slightly longer than that of the photoluminescence, as illustrated by the spectrum of **21** in Figure 4. This small bathochromic shift is by far the most common difference between tribo- and photoluminescence spectra and has been noted previously.[16,48,72,80] In cases where there is vibrational structure to the emission,[48] the reason for the shift is clear: the emission takes place deep in the crystals and is absorbed as it passes through the material, reducing the observed intensity of the 0−0 band and shifting the apparent emission maximum to slightly longer wavelengths. Moreover, we have never observed this shift for metal-based compounds such as **17** and **22**, which have their excitation maxima well-separated from their emission maxima,[16,50] nor have we ever observed a shift to shorter wavelength.[16]

Other studies have revealed some peculiarities in the activity and tribophotoluminescence spectra of **12** and **13**. Previous workers[62] believed **12** to be emitting without fracture, excited by phonon coupling, as no cracks could be seen. However, the erratic, spiky emission as a function of time and the absence of triboluminescence under liquids (Table 2) suggests that micro fractures might have healed.[118,119] Others found photoluminescence and triboluminescence emission of **12** to be highly variable, with some samples exhibiting no photoluminescence at room temperature but a strong tribophotoluminescence.[39,80,120] The spectrum of **13** is also highly variable. A long-wavelength shoulder in its tribophotoluminescence was assigned to pressure-induced interactions[85,121] and short wavelength lines to vibronic structure and stress-induced changes in Franck−Condon factors.[80] Later spectra do not show the shoulder (Figure 3); the short-wavelength lines have been shown to correspond to N_2 lines and to be dependent on the material and force of the grinder.[72] Both **12** and **13** exhibit emission on heating that was found to be neither thermoluminescence nor triboluminescence and was thus called pyroelectric luminescence.[122] Our samples of **12** and **13** were moderately triboluminescent and photoluminescent and otherwise unremarkable.

Because there is no spectroscopic evidence of a discharge for **11**, **12**, and **17**−**23**, these materials could be excited instead in the same way as the luminescent centers of doped and X-irradiated zinc sulfide and alkali halides when they are deformed,[40,110] namely, by recombination of defects that are swept through the materials and to the surface by moving dislocations.

The spectroscopic data provides a preliminary classification of the materials studied by the most probable mechanism for triboluminescence excitation, as follows:

1. A discharge definitely occurs: **1**−**10**, **13**, and **15**.
   a. The discharge excites N_2 by electron bombardment, and the UV emissions of N_2 excite any photoluminescence of the solid: **1**−**4**, **7**, **10**, **13**, and **15**.
   b. The discharge excites both N_2 and the solid by electron bombardment: **5**, **6**, **8**, and **9**.
2. A discharge probably occurs: **14** and **16**.
3. There is no evidence for or against a discharge: **11**, **12**, and **17**−**23**. Excitation could be by a discharge or by defect recombination.

d. Triboluminescence in Atmospheres Other Than Air. The fact that some materials (e.g., **5** under helium) are no longer triboluminescent under some other atmospheres whereas others (**1**, **7**, **12**, **13**, **16**, **17**, and **22**) are seems initially to be inconsistent with a discharge mechanism, especially since the intensity of

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22 is similar under several different atmospheres. We will first consider the properties of the gases or vapors and solids necessary for a discharge and its observation and then whether the results indicate that a discharge is necessary for triboluminescence.

The ionization potentials at first suggest helium to be the best choice for quenching triboluminescence, as some ionization is necessary to initiate a discharge. The ionization potentials are helium, 24.59 eV; sulfur hexafluoride, 19.3 eV; argon, 15.8 eV; dinitrogen, 15.7 eV; and carbon dioxide, 13.77 eV.[65,102,123] However, the dielectric strengths, or resistances to discharge, of these gases are in a very different order. At a pressure of 1 atm, argon and helium break down in the lowest electric field; dinitrogen, air, carbon dioxide, and oxygen in a field about double that strength; and sulfur hexafluoride in a field about 5 times that of helium, high enough that it is used to prevent breakdown in transformers.[124−126] Atoms and molecules with the richest density of electronic and vibrational states and highest mass dissipate the energy of the developing electron cascade, so that a higher electric field is required to push the random electron emissions into a full-scale discharge. Ionization potential and electron affinity play an additional role, as do the shape and nature of the charged surface.[126] Sulfur hexafluoride provides all of the features needed for high dielectric strength: many vibrational modes, high ionization potential, high mass, and high electron affinity (from the electronegative atoms). Thus, among the gases we used in this study, a discharge is most likely in argon and helium, less likely in air and carbon dioxide, and least likely in sulfur hexafluoride.

The ease of discharge increases as the pressure decreases for all gases, but it decreases again when the density becomes too low for conduction. The pressure optimum for gas-discharge triboluminescence is about 1 Torr in air and carbon dioxide and 100 Torr in argon.[67] The pressure of the gas or vapor in the developing cracks is unknown, but we anticipate that the pressures are close to the external pressure.

The electric fields generated by crystal fracture have been shown to be more than sufficient for discharge for all of the gases studied. Helium, dinitrogen, dioxygen,[127] air, and sulfur hexafluoride[123] all produce both electrical discharge and photon emission during the failure of adhesives. Dickinson[115] estimates that electrons are emitted on fracture of filled polymers in a field of 10^4–10^7 V cm^{-1}. Chandra and Zink estimate the field on fracture to be 1.26×10^6 V cm^{-1} for lithium sulfate hydrate[18] and 10^5 V cm^{-1} for some organics.[23] These fields are sufficient for dielectric breakdown of all of the gases used in the anticipated range of pressures; even sulfur hexafluoride will undergo breakdown in an electric field of less than 10^5 V cm^{-1} at 1 atm.[123,124,126]

For light emission to be observed from the gas itself, the energy of the cascading electrons must be sufficient to excite the gas molecules electronically during collisions. Of the gases that we used in addition to air, clearly helium is least likely to be excited by a discharge: its excitation energy is 21 eV, compared to 12 eV for dinitrogen[128] and 8 eV for carbon dioxide.[129] Still, the discharge energy is sufficient to excite helium photon emission in fracture of some materials, such as nonphotoluminescent adhesives[127] and minerals.[65] The energy of the electrons emitted by filled polymers when they were fractured ranged from 0 to over 1000 V.[115] These observations suggest that materials might produce different ranges of electron energies and thus excite a small or large fraction of helium atoms.

The light emissions from the gas must also be intense enough in the visible region of the spectrum to be observed. The triboluminescence emission in air comes from an electronically excited state of neutral dinitrogen,[59,128] which emits between 265 and 545 nm (it is extremely weak beyond 482 nm). Comparable emissions are observed for argon and neon to beyond 800 nm.[38,102,130] However, both helium and carbon dioxide have low luminous efficiencies (lumens per watt).[124] Visible emissions of carbon dioxide have been assigned to a transition from a bent triplet excited state to the linear singlet ground state.[131,132] High vibrational excitation of at least one of the states is required for these transitions, and thus, carbon dioxide's emissions are very weak. The weak luminescence might account for the facts that the lightning triboluminescence of barium chlorate disappears under carbon dioxide[133] and that of pure alkali halides is weakened.[67] Helium's emissions in both the UV and visible regions are also weak;[102] triboluminescence in helium has been detected by spectrometer and PM tube and is weaker than that in air.[65,127] Sulfur hexafluoride permits some discharge when tape is peeled, but no significant light emission[123] except from residual dinitrogen.[3] Neon, on the other hand, is highly luminous and has been shown to substitute effectively for air to give its characteristic red discharge emission when sucrose (**1**)[36] or frozen *cis*-4-octene[101] is fractured in it. Argon gives intermediate intensities, as the triboluminescence of **1** and alkali halides are weaker under argon than air[67] but that of lithium fluoride is higher at 1 atm.[67]

Of the samples that we tested under other atmospheres, only **5** has visible triboluminescence in air that consists entirely of emission from the gas. After it is recrystallized under helium, **5** produces no triboluminescence, but the activity returns when air is admitted to the sample. These observations are consistent with a discharge mechanism for excitation of **5**, with the emissions under helium being too weak to be seen. We would expect **5** to exhibit little or no activity under carbon dioxide as well. **1**, **2**, **6**, **8**, and **9** were not tested

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under helium but are similar in every other respect. We would expect all of them to produce red triboluminescence under neon similar to that of **1**.[36]

In contrast to **5**, the materials that are themselves photoluminescent in the visible region, namely, **9**, **12**, **13**, **16**−**18**, and **22**, continue to triboluminesce after they have been recrystallized under helium, argon, or carbon dioxide (or even sulfur hexafluoride for **22**). In addition, **7** has no N_2 lines in its emission under carbon dioxide.[63] The UV emissions of helium or carbon dioxide are likely to be too faint either to be seen or to be responsible for photoexcitation, but the electrons can excite the material directly. The photoluminescence of **3**−**23** can be excited by less than 5.4 eV, much less energy than for the gases. Thus, sufficient energy should remain in the discharge for electron bombardment to excite the photoluminescence of the materials. With polymers, so much energy is available during fracture that bonds rupture and release neutral and charged fragments from the surface.[112,134] **13**, however, also presents clear spectroscopic evidence for photoexcitation by absorption of the UV emissions of N_2 (Figure 3). If **13** were dependent only on photoexcitation for triboluminescence activity, the weak UV−vis emissions of helium and carbon dioxide should result in a significant reduction in triboluminescence activity; instead, the changes are small. On the other hand, if tribophotoluminescence is also excited by electron bombardment, then the loss of the N_2 lines from the emission would not reduce the intensity in the visible region by more than 1 unit on our crude scale. It is certainly possible, probable even, that electron bombardment of both gas and solid occur and, thus, that both mechanisms operate, with the proportions varying with the gas and the material. Similar conclusions can be drawn for **7**: under helium, the N_2 lines observed in air disappear, but tribophotoluminescence continues.[63] The possibility of excitation without discharge will be considered in section g, below.

The triboluminescence of other photoluminescent materials shows similar insensitivity to atmosphere, although there are inconsistencies in the observations. When placed under neon, 1-(9-anthracenyl)ethanol, which is similar to **16**,[48] retains its blue triboluminescence with increased intensity.[37] Harvey found that wintergreen candies, whose air emission is about half from N_2,[14,22] produce a greenish light under neon that is characteristic of the flavoring,[36] but **15,** with only 0.5% emission from N_2, emits both red and green light.[135] Color impressions are not entirely reliable when the eyes are dark-adapted; e.g., we see green flashes from **22** that are not present in the spectrum. **7** and chlorotriphenylmethane are still triboluminescent under carbon dioxide,[63] as is *N*-isopropylcarbazole under helium.[100] There is no effect of “gas nature or pressure” on the triboluminescence of **22** and similar compounds,[35] but one of these, pyridinium tetrakis(dibenzoylmethanato)europate,[58] is triboluminescent when placed under helium but not when recrystallized under helium.

A few studies have determined that triboluminescence emission spectra under gases other than air are consistent with discharge. Under argon, sodium chloride showed the characteristic emission of argon instead of N_2 lines, along with a broad emission.[38] Under sulfur hexafluoride, lithium fluoride showed only a broad continuum instead of the N_2 lines observed in air,[136] and ammonium tartrate gave only weak N_2 lines ascribed to N_2 trapped in the crystals (it produced an argon spectrum under argon).[3] Granite emitted the spectrum of N_2 in air and the characteristic emission spectra of argon and helium when broken under those atmospheres.[65] **7** and chlorotriphenylmethane under carbon dioxide produced just their tribophotoluminescence, although part of their emission under air was from N_2.[63] Manganese complexes lost the N_2 lines in their triboluminescence spectra when they were vacuum degassed.[137] Such experiments are consistent with our interpretation of the persistence of tribophotoluminescence under gases that do not produce sufficient UV light to excite the tribophotoluminescence, namely, that electron bombardment also excites the materials.

The observations of triboluminescence activity under other gases suggest the triboluminescence mechanisms are the following:

1. A discharge definitely occurs, and gases contribute their own visible emission: **1, 5**, and possibly **16**.
2. A discharge might occur, but excitation of tribophotoluminescence is via electron bombardment of the solid or deformation luminescence: **7**, **9**, **12**, **13**, **16**−**18**, **22**. Excitation by UV emissions of the gas might also occur, especially for **7** and **13**.

Let us consider the possibility that the added liquids (“under 2-propanol” and “under hexane” in Table 2) exert their effect on triboluminescence activity via their vapor, i.e., that the liquid incursion into the cracks is too slow to provide a liquid barrier to discharge (see section e). The liquid vapors probably have dielectric strengths between those of carbon dioxide and sulfur hexafluoride, with hexane more resistant to discharge than 2-propanol because of its higher ionization potential (just under 12.6 compared to 10.95 eV[138]) and more numerous vibrational modes. During the period of incursion of hexane and 2-propanol vapor into the crystals, the liquids will seal the cracks, but equilibrium will not be attained. The pressures will thus be less than their vapor pressures, about 150 and 40 Torr at room temperature, respectively,[102] plus the pressure of dissolved air. Some heating will occur during fracture, but the rate of evaporation will be too slow to significantly raise the pressure. Molecular fragments might also be part of the atmosphere in the crack. The lower pressure will reduce the field needed for discharge and could increase the discharge current.

Hexane and 2-propanol vapors require at least 7 eV for excitation (absorption maxima of 180 nm or less [138]). Although sufficient energy is likely to be available for excitation, these compounds are unlikely to exhibit any photoluminescence beyond 220 nm that could be seen or that could excite tribophotoluminescence. Thus, because the triboluminescence of **1**−**12** is quenched by the vapors, we can conclude that their triboluminės-

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cence is dependent on a discharge. For **1**, **2**, **5**, **6**, **8**, and **9**, solvent vapors produce no visible emissions; for **3**, **4**, **7**, and **10**−**12**, either solvent vapors do not produce UV emissions suitable for photoluminescence excitation or most of the discharge energy has been "squandered prematurely"[125] in exciting vibrational (and even electronic) modes of the vapors, leaving some (for **16**−**18**, **20,** and **22**) or all (for **3**, **4**, **7**, and **10**−**12**) of the electrons with insufficient energy to excite the material.

If the liquid vapor is responsible for quenching triboluminescence, it is difficult to understand why the response differs for liquid that saturates the crystals during recrystallization ("under mother liquor" in Table 2) from that added ("under 2-propanol" or "under hexane"). One needs to assume for **13**−**23** that enough energy remains in the discharge for the electrons to excite the photoluminescence of the crystal or that sufficient air remains to provide the UV emissions to do so. Yet these compounds are not significantly different in excitation energy from **3**, **4**, **7**, and **10**−**12**, which are not triboluminescent under either 2-propanol or hexane, nor are they more likely to have air trapped in the crystals. Even more disconcerting is the observed sensitivity to the identity of the vapor, as the triboluminescence activities of **7** and **12** persist under helium but not the liquid vapors and those of **17** and **20** disappear under hexane but not 2-propanol. These borderline cases might reveal a gradation in properties among the solids and the vapors. For example, materials whose tribophotoluminescence is reduced (**16**, **18**, **20**, and **22**) or eliminated (**3**, **4**, **7**, and **10**−**12**) by liquid vapor could share a poor ability to generate an electric field, so that a discharge with sufficient energy to excite the solid might only occur for a small fraction of the available sites. The vapor might dissipate the energy into excitation of its vibrational and rotational modes. If so, hexane, with the higher vapor pressure and most modes, is expected to be more effective at quenching triboluminescence than 2-propanol, exactly as observed with **17**, **18**, and **20**. In contrast to the hexane and 2-propanol vapors, gases such as helium and argon would dissipate very little energy and thus leave plenty for excitation of the molecules, as is observed for **12**, **13**, **16**, **17**, and **22**. Thus, **12**, **17**, and **20** might be producing electric fields barely sufficient for a discharge, so that some atmospheres are able to dissipate the energy and prevent excitation of the molecules, or prevent dielectric breakdown, whereas others needing less electric field for breakdown (e.g., helium) continue to produce a discharge with adequate residual energy and thus triboluminescence.

Explaining the effect of liquid on triboluminescence by assuming that only vapor intervenes requires far too many assumptions and fine distinctions for comfort. We next considers the alternative, that liquid flow into fissures in the crystal quenches triboluminescence.

If the vapors are responsible for changes in triboluminescence activity under liquid, our observations suggest that the mechanisms are as follows:

1. A discharge definitely occurs: **1**−**12**.
    a. Liquid vapors fail to provide sufficient visible emission: **1**, **2**, **5**, **6**, **8**, and **9**.
    b. Liquid vapors fail to provide sufficient discharge energy or UV emissions to excite the photoluminescence: **3**, **4**, **7**, and **10**−**12**.
2. A discharge probably occurs: **17** and **20**.
3. There is no evidence for or against a discharge: **13**−**16**, **18**, **19**, and **21**−**23**. Excitation could be via electron bombardment of the solid (**13**, **14**, and **18**) or deformation luminescence (**16**, **19**, and **21**−**23**).

e. Triboluminescence under Liquids. The disappearance of triboluminescence upon the addition of liquids, as exemplified by **1**−**12** in Table 2A, has been only rarely observed prior to this study. Wedgewood,[139] Longchambon,[17] Harvey,[36] Wick,[140] and Wolff [21] observed that the triboluminescence of **1** persisted under water and other liquids with reduced intensity. Zink et al.[12] were able to quench emission by vacuum-degassing the crystals before breaking them under argon-stripped benzene. Wintergreen candy, whose intense triboluminescence emission is dependent on the discharge of sucrose, does seem to lose its triboluminescence in water, as observed by chewers.[141] Tartaric acid and its salts lost intensity under liquids,[105] as did salicylamide.[104] Yet, the triboluminescence activities of a variety of europium salts, including **22**, were unaffected by 2-methylpentane,[35] hexane, and water.[142] **19**, whose triboluminescence we were unable to quench, was inactive when not free of the solvent it was initially grown from, aqueous acetic acid,[49] and 1-(9-anthracenyl)ethanol, similar to **16**, was inactive under water or hexane.[48] Our observation that stirring was necessary to stabilize activity for some materials suggests that variations in stabilization time might be responsible for discrepant reports about the effect of liquids on triboluminescence. Brady and Rowell[65] observed emissions from hydrogen molecules and atoms when they fractured granite under water; clearly tribochemistry had occurred. To our knowledge, the experiments presented here represent the first systematic evaluation of the effect of liquids on the emissions of triboluminescent materials.

To understand the effect of adding liquids, let us initially assume that the liquids flow very rapidly among the crystals and into the developing cracks, excluding air bubbles and creating a physical barrier to any discharge. The ability of 2-propanol and hexane to quench the triboluminescence activity of **1**−**12** correlates well with the evidence for discharge, namely, the presence of N_2 lines in the spectra of **1**−**10**. Still, the correlation is far from perfect as **13**−**15** and possibly **16** also produce N_2 lines and **11** and **12** might not. Thus, a discharge is the most likely mechanism for **1**−**12**, with liquid 2-propanol and hexane preventing the discharge.

The inability of 2-propanol and hexane to quench the triboluminescence of **13**−**23** presents a serious challenge to both discharge models. The liquids do have some effect, though. **16**, **17**, **20**, and **22** exhibit lower intensities under both 2-propanol and hexane than in air (Hurt et al.[35] observed no effect of liquid on **22**). The triboluminescences of **17** and **20** are quenched by hexane, and that of **18** is significantly reduced, yet 2-propanol has no effect. The reason for these differences might lie in the rate of incursion.

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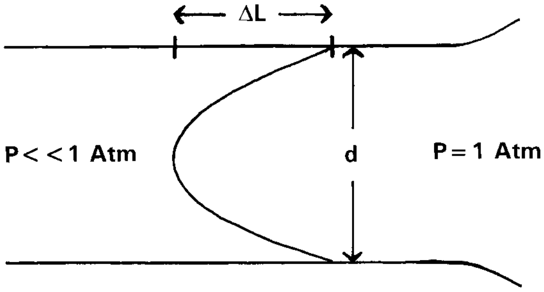

Figure 5. Model for fluid flow into a crack.

To quench discharge triboluminescence, liquid must flow into the cracks as fast as the cracks propagate, excluding air bubbles and creating nonconducting liquid barriers (discharges through condensed media require much more energy[124,143]). If, however, the liquid flows more slowly than the crack propagates, the liquid front will merely seal the crack. There will be some gas inside, i.e., vapor from the liquid, atmospheric gas molecules that have been trapped in the crystals,[38] and molecular fragments released into the cracks,[30,144] but the pressure will certainly be lower than that in the surroundings. The liquid front will then be driven by the 1 atm of pressure outside the crystal against the low pressure inside.

A simple model for estimating the rate of incursion of the liquid into the crystal is shown in Figure 5. For a planar crack of uniform spacing d, the velocity v of the liquid driven by pressure difference ΔP is given by[145]

$$v = \frac{\Delta P d^2}{8 \Delta L \eta} \tag{1}$$

where η is the viscosity and ΔL is the length over which the liquid front extends. The crack geometry, and thus d in eq 1, should be similar under the two liquids, but the parameter describing the shape of the leading edge, ΔL, might vary with liquid viscosity or surface tension or the nature of the new surface. A lower limit of 1 nm can be set on d, as Dickinson et al.[6] have shown that cracks less than 1 nm exhibit tunneling rather than discharge. Assuming a crack spacing d of 10 nm, a high ΔP of 1 atm, and a range of ΔL from 100 to 10 nm gives a velocity range for the liquid front of 40−400 cm s^{-1} for hexane and 6−60 cm s^{-1} for 2-propanol. Because of its lower viscosity,[102] hexane will flow into the crack nearly 10 times faster than 2-propanol (or even faster if ΔL is also dependent on η). The observation that **17** and **20** continue to triboluminesce under 2-propanol but not under hexane alone is dramatic enough to provide confirmation that liquid can quench triboluminescence by flowing into a crack and thus that the triboluminescence of **17** and **20** is dependent on a surface phenomenon such as a discharge. Zink et al. also found viscosity to be important, as **1** continued to triboluminescence with full intensity under viscous Nujol but exhibited reduced intensity under mobile liquids such as benzene and chloroform.[12] Is the flow rate, however, really fast enough to fill the cracks as they are formed?

The maximum velocity of crack formation will be the shear speed of sound in the crystal, which might vary with direction in these polar crystals. Measured crack velocities are usually less than the shear speed of sound,[146] because cracks stall at defects and then zigzag to produce rough surfaces.[147,148] In addition, cracks will decelerate as energy is lost to deformation and heat in these soft materials. Energy can also be lost to the production of sound, although some of the sound might feed back into the cracking process.[149] In these mostly piezoelectric materials, energy will also be consumed in the separation of charge. Crack velocities for **1**−**23** should be similar to those measured in organic polymers, namely, 1×10^5 cm s^{-1} in polystyrene,[102] 3×10^4 cm s^{-1} in polycarbonate,[150] and $(2-6) \times 10^4$ cm s^{-1} in PMMA.[149] Although polymers might be harder, they will lose additional energy in bond-breaking. Thus, we estimate the actual crack velocity in **1**−**23** to be on the order of 10^4−10^5 cm s^{-1}, far faster than our estimate of the liquid velocity. It is hard to imagine how a liquid can possibly succeed in quenching triboluminescence. However, we have made some significant assumptions. If our estimates of crack velocity were high by a factor of 10−100, and/or our estimates of liquid flow rate low by a factor of 10−100, differences in the rate of liquid incursion into the cracks could explain the differences in triboluminescence activity under liquids without abandonment of a discharge mechanism for **13**−**23**.

Materials do vary in their crack velocities in ways that might affect their triboluminescence activities. The hardest materials should have the highest crack velocity and thus the best chance of emitting under liquids. Qualitatively, the hardest materials in this study are **1** and **15**, but the triboluminescence of **1** is quenched by liquids. High crack propagation rates might be needed to develop adequate potential for discharge triboluminescence, as hard materials have been shown to exhibit more intense triboluminescence than similar softer materials.[151] Dissipation of crack energy into modes other than charge separation might be responsible for the observed differences in rate, but the possibility that a discharge is not necessary must be retained for those materials whose triboluminescence is not quenched.

Liquid flow could be faster than expected. Perhaps the liquid flow is not laminar, as assumed, but turbulent. For example, the low pressure inside the crack could cause the liquid to boil momentarily and splatter into the crack (again, hexane, with its lower boiling point, would enter more quickly than 2-propanol). Perhaps we have underestimated how large the cracks

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are (in arsenolite, they are estimated to be 100 nm[152]). Cracks larger by a factor of 10 would give a flow rate 100 times faster, enough to match the crack velocity. Perhaps the model is inappropriate for cracks that are only a few molecules wide and have irregular surfaces. Although the properties of freshly formed surfaces could also affect the liquid flow, there is no evidence that they do. In particular, **1**, **15** and **17** with the most polar surfaces should be readily wetted by 2-propanol, but the triboluminescence of **15** and **17** persists under 2-propanol.

The reductions in intensity observed for **16**−**18**, **20**, and **22** could have simple causes. **16** was partially dissolved during the experiments, and the lowered intensity could be a consequence of fewer emission events. For others, lubrication of the crystals by the liquid, or powdering by excessive grinding, could reduce the effective grinding force and cause the observed reductions. There is no obvious surface or bulk property of the materials that is consistently different for the quenched (Table 2A), reduced, and unquenched (Table 2B) materials, nor can mechanical problems explain the differences between hexane and 2-propanol. Thus, we took additional measures to exclude air, as described below.

If a liquid barrier quenching discharge is the source of the effect of covering the materials with liquid, then we can conclude the following:

1. A discharge definitely occurs: **1**−**12**.
2. A discharge probably occurs.
   a. The intensity is reduced under liquids: **16**, **18**, and **22**.
   b. The intensity is zero under hexane: **17** and **20**.
3. There is no evidence for or against a discharge: **13**−**15**, **19**, **21**, and **23**.

f. Triboluminescence under Recrystallization Solvent. To further examine the possibility that a nonconducting liquid barrier is responsible for quenching triboluminescence, we reduced the effects of trapped air and flow rate by examining the triboluminescence of these materials upon recrystallization, under their mother liquors, without ever exposing the samples to air. When Longchambon did a similar experiment, he noted that cinchonine sulfate and hydrochloride and hippuric acid (similar to **11**) lost their triboluminescence activity under their recrystallization solvents.[17] Moreover, **19** is inactive if it is not free of the solvent from which it is initially isolated, aqueous acetic acid.[49]

As expected, the tested materials whose triboluminescence was lost when liquids were poured over them (**1**−**12**) also failed to triboluminesce under their mother liquors (Table 2, "under mother liquor" and "recrystallization solvent"). Thus, we can conclude with confidence that their triboluminescence was dependent on their surface and presumably on a discharge. In addition, the loss of activity for **13**−**15**, **18,** and **20** under mother liquor suggests that they too require a discharge for activity. **13**−**15** have already provided evidence for a discharge in their spectra, which have partially absorbed lightning lines (see section c). **18** and **20** provided a preview of their response to exclusion of air by mother liquor: **20** had no triboluminescence, and **18** much weaker triboluminescence when hexane was added. It appears that, for **13**−**15**, **18**, and **20**, the flow of liquids into the cracks was not fast enough to prevent discharge, but the liquid saturation obtained during recrystallization was able to prevent discharge and its consequent triboluminescence. Because the triboluminescence of **17** was quenched by hexane, we assume that it is similar to **18** and **20**.

Because the activities of **2**, **4**, **14**, and **15** failed to return upon drying ("after drying in air" in Table 2) and those of **7** and **11** barely did so, the conclusions drawn above must be moderated. **2** and **4** provide plenty of other evidence for a discharge. **15** no doubt lost water of hydration and produced a different salt; it has also been shown to lose its triboluminescence and become opaque when heated,[1,153] and **17** would no doubt behave similarly. **4** and **7** showed evidence of impurities in their triboluminescence and photoluminescence spectra; pure **7** has already been shown not to be triboluminescent.[98] **14** has the deep brown color of an impure amine. **11** has three polymorphs, only one of which is noncentric and triboluminescent;[61] we might have produced primarily a different form on recrystallization. Thus, we tentatively ascribe the loss of triboluminescence activity after recrystallization by **2**, **4**, and **14** to the removal of impurities necessary for the activity or to the production of a different crystal form and that of **15** to loss of water of hydration. The significant reductions in the triboluminescence intensities of **7** and **11** no doubt have similar causes. Except for the loss of activity on recrystallization, the materials whose triboluminescence spectra were clearly the result of impurities (**4**, **7**, and **20**) behaved much like the materials whose spectra were from the host material.

Of the 23 materials, only **16**, **19**, and **21**−**23** continue to be triboluminescent when saturated with liquid, even though the only air they have been exposed to is that dissolved in the solutions from which they were grown. **19** is not triboluminescent when the original precipitate is still wet with its acetic acid−water mother liquor,[49] but it is moderately triboluminescent when dried. This observation indicates either that water or acid has a different effect on its triboluminescence than other solvents or that the initial crystal form is different. Two possibilities exist for the excitation of **16**, **19**, and **21**−**23**. Electron bombardment could still occur by a discharge through solvent vapor or air desorbed from the lattice if liquid flow cannot keep up with crack propagation. Such gas desorption was observed to support discharge by **1** under high vacuum.[33] This mechanism would be especially likely if stoichiometric amounts of air were cocrystallized, but calculated and measured crystal densities are the same for **16**[48] and **22**.[50] It seems far more likely that the triboluminescence of these materials occurs via a mechanism that does not require a discharge, such as that discussed in section g below.

Thus, the disappearance of some triboluminescence when the material is not isolated from its mother liquor suggests the following mechanisms:

1. A discharge definitely occurs: **2**−**4**, **7**, **10**−**13**, **18**, and **20**.

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2. A discharge probably occurs (based on other experiments): **1**, **5**, **6**, **8**, **9**, **14**, **15**, and **17**.
3. There is no evidence for a discharge: **16**, **19**, and **21**−**23**.

g. Non-Discharge Mechanisms: Deformation Luminescence. It has been shown that the triboluminescence of doped zinc sulfides, irradiated alkali halides and some semiconductors is caused not by a discharge upon fracture but by recombination of oppositely charged, energetic defects as the dislocations sweep them into collision during deformation.[40,42] The triboluminescence excitation occurs throughout the bulk of the material and thus is insensitive to liquids or other atmospheres: manganese-doped zinc sulfide is active under water[154,155], as is doped strontium aluminate under several liquids.[156] **16**, **19**, and **21**−**23** could emit by this mechanism. It will be more difficult to provide positive evidence for this source of excitation in **16**, **19**, and **21**−**23** than it was in the doped zinc sulfides and irradiated alkali halides. For them, the primary evidence was spectroscopic, namely, that the triboluminescence spectra were less like the photoluminescence spectra than the electroluminescence or thermoluminescence spectra, both of which are known to be characteristic of defects and their recombinations.[3,40,157−159] Unfortunately, the intense photoluminescence of **16**, **19**, and **21**−**23** would mask any spectral peculiarities from low-concentration defects. Moreover, most of the defects in molecular crystals such as **16**, **19**, and **21** have been shown to be low-energy vacancies, i.e., missing molecules.[160]

Electronic examination of crystals of small organic and inorganic molecules provides evidence that, indeed, the needed trapped energetic defects can be present in materials such as **16**, **19**, and **21**−**23**. Although small molecules have not been studied in as great detail as polymers, crystals of photoluminescent molecules with similar (anthracene) or slightly larger [oligo(phenylvinylidene)s] molecular weights can be strongly electroluminescent[161] or can behave as photovoltaic or photoconductive devices (the complementary phenomena).[162] Defects can also be detected by conductivity or restrictions to it,[163] or by their ability to trap excitons,[164] and are significantly enhanced by chemical impurities.[165] Thus, molecular crystals also have defect structures such as those of the doped alkali halides and zinc sulfide: electrons and holes are trapped in the lattice at crystal defects, grain boundaries, and chemical impurities.[162] The electron and holes can be released by the motion of the dislocations under the crystal strain, just as they are released by the applied voltage in electroluminescence. The result will be the same: defects recombine, annihilating each other in some cases, providing sufficient energy to cause electronic excitation and thus luminescence.[166] The spectral characteristics of the defect sites might appear different using different modes of examination, because higher-energy input will activate electrons and holes in deeper traps. The energy input in triboluminescence is currently unknown, as are the nature and energy of the defects in these materials, but spectral evidence for this mechanism might eventually be found for materials such as **16**, **19**, and **21**−**23**.

It is curious that **16**, **19**, and **21**−**23** are noncentric; this property has not been considered important to deformation luminescence, although zinc sulfide is also noncentric. An alternative mechanism for excitation suggests itself from this observation. As the crystals are deformed, they develop a voltage. If the piezoelectric field reaches the threshold for inducing motion of some mobile defects, it could excite the electroluminescence, thus rendering the sweeping of defects by strain-induced dislocation motion unnecessary. In materials of high piezoelectricity, this piezo-induced electroluminescence seems to be a viable mechanism. This is exactly the tribo-induced electroluminescence mechanism proposed by Meyer et al. for doped zinc sulfides.[40] The evidence for the doped materials is quite strong. For example, the triboluminescence spectrum of ZnS:10^{-3} Cu,Cl has a strong band that is absent from its photoluminescence emission but characteristic of its electroluminescence.[167] In addition, the lifetime of its photoluminescence is 7 ms, much longer than the lifetimes of 17 and 26 μs for triboluminescence and electroluminescence, respectively.[40]

It is unlikely that the emission spectra of **16**, **19**, and **21**−**23** would be any different whether they are excited by UV−vis radiation, electron bombardment, or applied voltage, as they will all be dominated by the same intense chromophores. Too little is known about these materials to do more than speculate on the nature or energy of any defects. Electrons are commonly among the defects found in aromatic compounds. They are likely to be in shallow traps (antibonding or nonbonding orbitals) and thus might migrate (or hop) in a small induced field. Chemical impurities are certainly present as none of the materials were recrystallized more than a couple of times. **22** appears to be crystallographically disordered. In addition, charge defects are likely in both **22** and **23**, from incorporation of substitute ions or neutrals during synthesis or on standing (**23** develops a strong amine odor after many months). Although these molecule-sized defects are unlikely to move themselves, they might provide electrons or holes. Triboluminescence lifetimes are determined by both mechanical relaxation and photoluminescence lifetimes and are about 2 μs for **9**, **12**, **13**, and **18**[94] (**22** has a phosphorescence lifetime of about 600 μs). Measurement of the piezoelectric constants and analysis of the electrooptical

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properties of these materials would ascertain the viability of such a mechanism.

Even materials whose triboluminescence is sensitive to liquids might depend on deformation-induced processes before and during fracture. Observations of photon and particle emissions during fracture provide overwhelming evidence that dislocation pop-out provides a source of energetic electrons to bombard the surface for alkali halides,[113] explosives,[168] and zinc sulfides.[169] The phenomenon is sometimes called surface electroluminescence,[99,169] although it is really a form of cathodoluminescence. In opaque materials, only the surface activity is seen.[170,171] Thus, recombination of mobile defects could contribute to the overall emission even when discharge is indicated.

Conclusions

The experimental results presented in this and many other papers illustrate effectively a diversity of behavior of triboluminescent materials that has confounded simple interpretation. No one mechanism will explain all of the light emissions that have been observed under stress or fracture, even for only 23 materials. Two clearly distinct mechanisms can be identified by this study.

1. Many materials, including most of those examined here, exhibit triboluminescence that requires a discharge through air or other surrounding gas. The electric field that makes the discharge possible is usually generated by the piezoelectricity of the material, although local dissymmetries from impurities and defects are also a possible source. For prima facie evidence of a discharge, we accepted any of the following: the presence of N_2 emission lines in the triboluminescence spectrum that exhibit absorption, the disappearance of the triboluminescence under liquids, and the disappearance of triboluminescence under a poorly luminescent gas if the visible emission is entirely from the gas (or the emission of red light under neon).

Three separate excitation modes involving a discharge were observed in this study:

a. Excitation of the surrounding gas by electron bombardment. **1** and **2** exhibit spectra consisting only of the lines from gas emission, and their triboluminescence is quenched by liquids.

b. Excitation of the photoluminescence of the material by electron bombardment. Photoluminescent **5**, **6**, **8**, and **9** exhibit N_2 emission lines; they are incapable of absorption of those lines and, thus, of mechanism 1c. **7**, **12**, **13**, and **17** might be excited this way, as their triboluminescence persists under helium and carbon dioxide, neither of which can excite them by mechanism 1c. Their triboluminescence is quenched by liquids.

c. Excitation of the photoluminescence of the material by absorption of the UV emissions of the excited gas. **3**, **4**, **7**, and **13**−**15** exhibit N_2 emission lines in their triboluminescence spectra with relative intensities consistent with absorption by the material. **11**, **12**, **15**, **17**, **18,** and **20** might be excited this way, as their spectra contains no evidence of N_2 lines but they lose their activity under liquids.

These three discharge mechanisms are not mutually exclusive. N_2 lines (1a) occur with mechanisms 1b and 1c, and **12**, **13,** and **17** show evidence of excitation by both mechanisms 1b and 1c.

2. Some materials exhibit triboluminescence from processes within the crystal, possibly the release of energy from recombination of defects as they are swept to complementary sites either by deformation or by piezoelectric polarization of the crystal. **16**, **19**, and **21**−**23** continue to exhibit triboluminescence under other atmospheres and under liquids and give no evidence of gas emission lines in their spectrum. **16** occasionally exhibits traces of lines from gas discharge, a discrepancy that might indicate participation from mechanism 1 or, more likely, a parallel discharge between different materials.

To our knowledge, **16**, **19**, and **21**−**23** are the first simple molecular crystals to exhibit what appears to be deformation luminescence, i.e., luminescence that depends on processes inside the crystal rather than on the surface. Hurt et al. also found the triboluminescence of **22** to be insensitive to its surroundings.[35] Other materials, such as tetrahedral manganese complexes and other lanthanide complexes, also show evidence of this mechanism by the persistence of their triboluminescence under liquids.[64,142] In other materials dependent on deformation, fracture has been shown not to be necessary for triboluminescence. Most emit on plastic deformation, and a few emit on elastic deformation. Further experiments are clearly indicated to determine whether these materials indeed emit on deformation alone. If they do, their activity will be intact under high vacuum, and emission will be initiated by strain alone.

One curious observation requires comment. A comparison of the intensities here and in other measurements indicates that there is a maximum intensity for materials that yield only a gas discharge emission, with sucrose (**1**) producing about the highest intensity yet observed. **1** is the brightest of about 50[18,19,60] lightning emitters examined by Zink's group using PMTs. In this study, the materials whose visible emissions were entirely from lightning, namely, **1**, **2**, **5**, **6**, **8**, and **9**, had the same intensities in air by visual comparison. However, the photoluminescent materials such as alkaloids and uranyl salts can be significantly brighter, even to an UV-sensitive PM tube.[18,19,23,60] The brightest of all are the materials that are not dependent on a discharge. None of the investigations controlled the applied force effectively or determined the photoluminescence or PM-tube efficiency. Thus, the real efficiencies are not known. It is important to determine why discharge emitters do not reach the triboluminescence intensity that photoluminescent materials do so that intensely triboluminescent materials can be developed.

A great deal of attention is being given these days to organic semiconductors. As these studies are being done, it would be worthwhile to investigate the triboluminescence of the materials. Conversely, **16**, **19**, and **21**−**23**

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might have the defect structure needed for semiconductor behavior and might have some potential in electroluminescent or photoconducting devices, alone or as dopants, although their triboluminescence might create interference. Certainly, their electronic properties are likely to be intriguing.

In accord with the statistical principles embodied in Occam's razor,[172] we have selected what we believe to be the simplest explanation for triboluminescence in these materials. Triboluminescence is usually a mixture of gas discharge emission, photoluminescence excited by the gas emissions, and photoluminescence excited by electron bombardment, with one mechanism producing most of the light, depending on the material and the gas. Some materials, even molecular crystals of small molecules, do emit without involvement of the surface, most likely by recombination of energetic defects during deformation.

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