Triboluminescence

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Triboluminescence (TL) is the emission of light caused by application of mechanical energy to a solid. The word was coined by Wiedemann in 1895[1] and takes its root from the Greek "tribein", to rub. The word is of broad general usage and covers a variety of mechanical methods of excitation, spectroscopic origins of the luminescence, and mechanisms of excitation. All of these aspects of TL will be discussed in this Account.

The history of TL is long and varied. The first recorded observation of TL known to the author is contained in Francis Bacon's "The Advancement of Learning".[2] Bacon reported that lumps of sugar emitted light when scraped. The triboluminescence of sugar was known to other early writers, including Boyle, who observed that "hard sugar being nimbly scraped with a knife would afford a sparkling light".[3] The best examples of TL using common household substances are demonstrated by grinding sugar or certain candies such as wintergreen lifesavers in a dark room.

A different form of TL, that caused by the motion of mercury over a glass surface in a vacuum, was first reported by Picard in 1675.[4] This type of TL was also independently reported by Hauksbee in 1705[5] and by Newton in 1718.[6] Other early studies of historical interest include the reports of Muschenbrock in 1661[7] and Wiedemann and Schmidt in 1895.[1]

The mechanical energy which is used to excite TL can take a wide variety of forms. The two most common forms are anisotropic pressure by grinding or crushing crystals and the motion of a fluid over the surface of a solid. Other important methods of excitation include thermal shock which causes strain, cracking or phase changes of a crystal, and rapid crystallization which also can cause strain or cracking. The most convenient method of exciting crystals or powders for spectroscopic studies is by crushing or grinding them against an optical window.

The borderline between TL and other forms of luminescence such as thermoluminescence or chemiluminescence is often not well defined. For example, the

mechanical energy applied to the crystal in the TL experiment could be converted to heat energy which in turn could cause either thermoluminescence or a chemical reaction producing a product in an excited electronic state. These effects will be respectively called tribo-induced thermoluminescence and tribo-induced chemiluminescence. Two trivial forms of TL are also covered by the definition of TL. The incandescent fragments produced when two hard objects are struck together or frictionally heated might be called TL. Electrical arcing produced by static electrification when dissimilar objects are rubbed might also be called TL. The luminescence caused by flowing mercury falls in the latter category. Most of the triboluminescent substances to be considered in this Account do not have such simple origins and explanations.

Triboluminescence links the spectroscopic, structural, mechanical, and electrical properties of solids. The two primary goals of current research are to elucidate the excited-state origins of the luminescence and to determine the mechanisms by which those states are populated.

Spectroscopic Determinations of the Origins of Triboluminescence

The TL of the solids studied to date has eight origins. In roughly decreasing order of occurrence they are crystal fluorescence,[8-10] crystal phosphorescence,[8,10,11] luminescence from nitrogen or other gases,[12-16] metal-centered luminescence,[8,17-21] luminescence from

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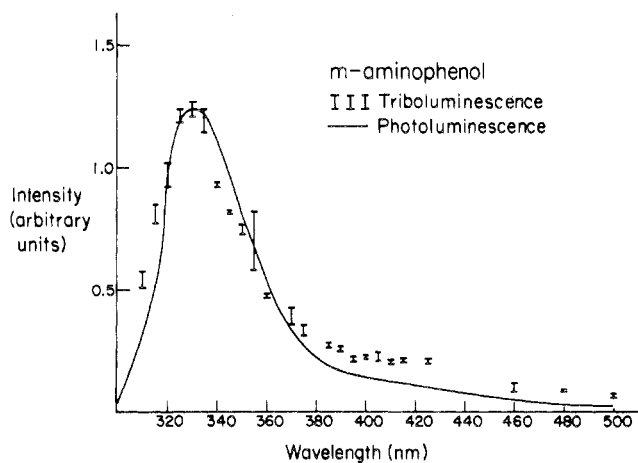
(1) G. Wiedemann and F. Schmidt, *Ann. Phys. (Leipzig)*, **54**, 604 (1895).
(2) F. Bacon, "Of the Advancement of Learning", 1605, G. W. Kitchin, Ed., J. M. Dent and Sons, London, 1915.
(3) E. N. Harvey, "A History of Luminescence", American Philosophical Society, Philadelphia, PA, 1957, Chapter 10.
(4) J. Picard, cited in E. N. Harvey, *Science*, **89**, 460 (1939).
(5) Fra. Hauksbee, *Philos. Trans. R. Soc. London*, **24**, 2130 (1705).
(6) I. Newton, "Optiks", 1718.
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(8) G. E. Hardy, J. C. Baldwin, J. I. Zink, W. C. Kaska, P. H. Liu, and L Dubois, *J. Am. Chem. Soc.*, **99**, 3552 (1977).
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(14) J. I. Zink, *Chem. Phys. Lett.*, **32**, 236 (1975).
(15) J. I. Zink, G. E. Hardy, and J. E. Sutton, *J. Phys. Chem.*, **80**, 248 (1976).
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(17) J. I. Zink, *Inorg. Chem.*, **14**, 555 (1975).

Figure 1. Tribofluorescence and room-temperature crystal photoluminescence spectra of *m*-aminophenol.

Figure 2. Tribofluorescence and room-temperature photoluminescence spectra of phenanthrene (top) and coumarin (bottom), demonstrating redistribution of vibronic intensities.

charge-transfer complexes,[8] and single examples of luminescence from free radicals[22] and possibly blackbody radiation[23] and conduction-band to surface-band transitions.[24] Combinations of several of the above origins contribute to the TL of some crystals.[8,18,23-25]

The best generalization of the type of TL which can be expected from a crystal is that it will be similar to the crystal photoluminescence (PL) at the same temperature.[8] The TL and PL spectra would be expected to be uniformly identical if the sole effect of the mechanical stress were the population of excited electronic states. The importance of the perturbations to the crystal and the emitting centers caused by the mechanical stress is evidenced by the differences between the PL and TL spectra which are usually observed.

Significant differences between TL and PL spectra are often found. There are crystals which are triboluminescent at room temperature which exhibit no photoluminescence at that temperature.[8,10,18] More commonly, a triboluminescent crystal will be photoluminescent, but the TL spectrum will contain new features which are absent in the PL spectrum. These new features may be emission bands which do not occur in the PL spectrum or changes in the relative intensities of bands in the TL spectrum compared to those in the PL spectrum. In the following discussions, the spectroscopic results are organized according to the origins of the most intense TL emission band.

Tribofluorescence. The photophysical process to be considered in this section involves emission from an electronic excited state with the same spin multiplicity as the ground state. The emission band width and any observed structure result from the nonzero probability of transitions to many vibrational levels of the electronic ground state. The TL excitation, unlike the PL excitation process, does not involve absorption of a photon

and is thus not necessarily a vertical electronic transition.

The TL and PL spectra should be identical within experimental error if they occur from the same molecule under the same conditions (temperature, pressure, neighboring molecules in the lattice). The three tribofluorescent molecules which exhibit the greatest known similarities between the spectra are resorcinol, *m*-aminophenol, and *p*-anisidine.[8] The TL and PL spectra of a representative example, *m*-aminophenol, are shown in Figure 1. The TL spectra are taken point by point.[26] The error bars represent one standard deviation of the measured intensities. Even in *m*-aminophenol, small dissimilarities are noted. For example, the intensity of the shoulder at about 420 nm in the TL spectrum is greater than that in the PL spectrum. This small difference could be caused by experimental errors in normalizing the spectra and accounting for the different instrumental responses. The most important similarities between the TL and the PL spectra in Figure 1 are the coincidence of the peak maxima at 330 nm and the very similar band shapes. The TL emission is assigned to the same electronic transition as that of the PL on the basis of these similarities. The transition can be further assigned as a fluorescence using PL spectroscopy. The TL of resorcinol and *p*-anisidine are also assigned as fluorescences.[8] Although the above three compounds are the only examples of tribofluorescence known to date which exhibit such close similarity to the PL, others can be expected to be found as the field develops.

The most common experimentally significant difference between TL and PL spectra is a marked change in the intensities of peaks in the main band. The TL and PL spectra of a representative example, phenanthrene, are shown in Figure 2.[8] The band maxima in both the TL and PL spectra occur at the same wave-

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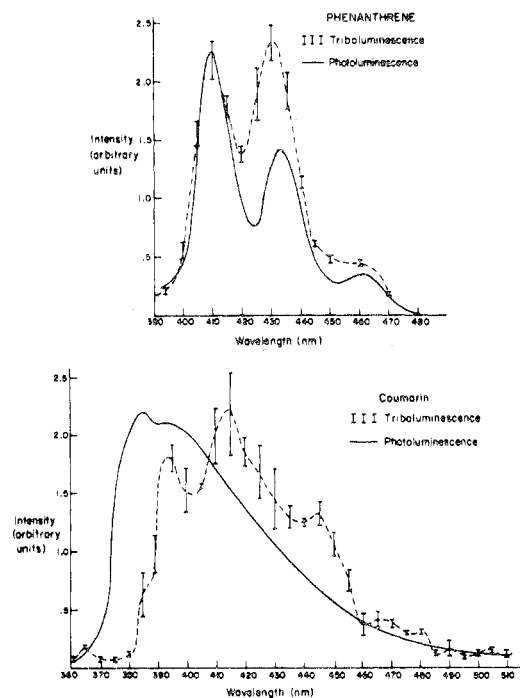
(26) The instrumentation is described in ref 18.

lengths (410, 430, and 460 nm), but the band intensities have a 1:1:0.2 ratio in the TL spectrum compared to a 1:0.6:0.2 ratio in the PL spectrum. The peaks at 410 nm were normalized to equal intensity in Figure 2 for display purposes. It is not known whether the TL band at 430 nm has gained intensity relative to the band at 410 nm as implied by the normalized intensities or whether the TL bands at 410 and 460 nm have lost intensity relative to the 430-nm band.

A more dramatic change in relative intensities of TL and PL peaks is found in the superposition of the TL spectrum and the room temperature photoluminescence spectrum of solid coumarin shown in Figure 2.[8] The maximum of the PL peak occurs at 389 nm and has been previously assigned to the $^1(\Pi^*,\Pi)$ fluorescence.[27] The maximum of the TL spectrum is the peak at 415 nm. At the 5-nm resolution of the TL spectrum, structure on the fluorescence peak can readily be resolved, in contrast to the much less structured photofluorescence peak. The average energy spacing between the peaks between 450 and 360 nm is 1630 cm^{-1}, within experimental error of the 1596-cm^{-1} C=C stretch.

In the spectra which have been studied to date, both the appearance of detailed structure and the changes in the relative intensities of emission bands appear to be related to changes in the Franck–Condon factors and thus to the changes in the vibronic intensities of the emission caused by the application of mechanical energy or pressure to the crystals in the TL experiment. Large changes in the vibronic intensity distributions in aromatic molecular crystal luminescence spectra caused by hydrostatic pressure are known from high-pressure studies.[28] In the TL spectra, the energies of the vibronic bands generally closely correspond to those in the PL spectra if the latter can be resolved.

The Franck–Condon enhancement of vibronic bands caused by the mechanical stress is prominent in many tribofluorescence spectra. Fluorescence, with a very short lifetime, can occur from molecules which are affected by the mechanical action at the time they are emitting. It is reasonable to expect that much longer lived emissions would not exhibit such effects because the relaxation of the mechanical action could occur before the molecules emit. However, some types of pressure-induced luminescence features require a time scale on the order of days in order to relax, probably because of the length of time required for the crystal to anneal at room temperature.[29] At the present time it is impossible to identify the exact pressure effect which causes the new TL spectral features. Elucidation of these effects will require the discovery and spectroscopic study of more examples of triboluminescent crystals.

Other explanations for changes in the relative intensities of the emission bands include (1) the appearance of new luminescent centers such as crystal defects or traps, (2) changes in the relative quantum yields of fluorescence and phosphorescence, (3) self-absorption of anti-Stokes vibronic emission bands, and (4) impurity effects. Because the grinding of the
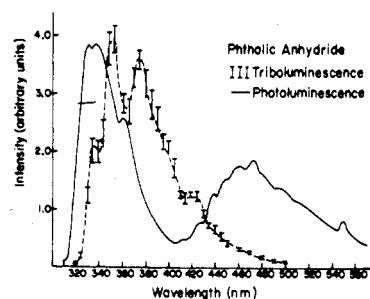
(27) P. S. Song and W. H. Gordon, *J. Phys. Chem.*, **74**, 4243 (1970); W. W. Mantulin and P. S. Song, *J. Am. Chem. Soc.*, **95**, 5122 (1973).
(28) H. W. Offen, "Organic Molecular Photophysics", J. B. Birks, Ed., Wiley, New York, N.Y., 1973, p 122.
(29) Reference 28, p 144.

Figure 3. Triboluminescence of phthalic anhydride, a crystal which is not photoluminescent at room temperature. The photoluminescence was recorded at 77 K.

crystals required to produce the TL is also conducive to the production of crystal defects, luminescence from traps or specific sites in the crystal is expected to be important. However, in all of the spectra studied to date, the new peaks which appear in the TL are well separated from the other peaks, with energy spacings on the order of the skeletal vibrations. Emission from traps is thus probably not the cause of the detailed structure or the changes in the relative intensities of the bands, although it may be responsible for the generally observed increased broadness of the TL spectra relative to the corresponding PL spectra. The possible effects of impurities on the spectra are more difficult to quantify. The fluorescence spectrum of microcrystalline phenanthrene has been shown to depend on the method of sample purification.[30] Because the TL and PL spectra were obtained from samples purified in the same manner, the differences between the spectra are probably not a direct result of impurities. However, as mentioned above, one of the effects of pressure in the TL experiment might be to produce traps whose presence and nature could be related to impurities in the sample. Spectral changes caused by the second and third categories have been identified.[8,17]

TL from Nonphotoluminescent Crystals. One of the most intriguing and unusual aspects of TL is the occurrence of TL from crystals which do not photoluminesce under the same conditions. TL from nonphotoluminescent crystals is not rare; it occurs from such diverse substances as mono- and disaccharides,[15] metal complexes,[18] and aromatic compounds.[8,10] The origin of the TL of some of these compounds has been shown spectroscopically to be different from the molecular crystal fluorescence considered in this section. The saccharides and aniline hydrochloride which exhibit nitrogen emission and the metals which exhibit metal-centered phosphorescence will be discussed in following sections.

The only spectroscopically studied example of tribofluorescence from a crystal which is not photoluminescent under the same conditions is phthalic anhydride.[8] Spectral assignments can be made because the compound is photoluminescent at 77 K. The room temperature TL spectrum is shown superimposed on the PL spectrum taken at liquid nitrogen temperature in Figure 3. The intense peak in the PL spectrum at 340 nm is a fluorescence. The phosphorescence maximum, with a lifetime of 800 ms, is centered at 470 nm. The fluorescence contains three resolved peaks at

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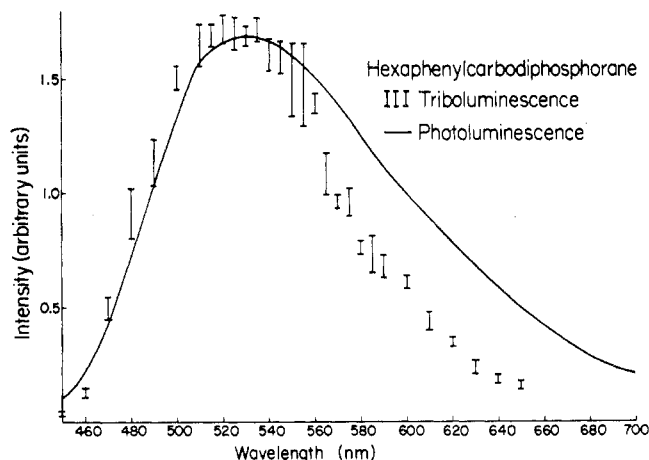
Figure 4. Tribophosphorescence and room-temperature crystal photoluminescence of hexaphenylcarbodiphosphorane, $(Ph_3P)_2C$.

333, 345, and 363 nm at liquid nitrogen temperature. The fluorescence spectrum is temperature dependent. With decreasing temperature, the intensity increases in the high-energy region of the spectrum. In the room-temperature TL spectrum, well-resolved peaks are observed at 335, 355, and 420 nm which are assigned to tribofluorescence. Only tribofluorescence is observed.

No definite explanation for the above observations can yet be offered. The observation of TL but not PL may be a result of an enhancement of the luminescence intensity when excited by mechanical stress relative to the intensity of photoluminescence. This enhancement may be related to the intensity redistribution in the vibronic peaks as discussed earlier. In support of this interpretation, the TL spectrum of phthalic anhydride occurs in the same wavelength region as the liquid nitrogen temperature photoluminescence, but differs markedly in detail. (No room temperature photoluminescence was detected.) Thus, the TL may result from enhanced vibronic emission. The vibronic bands are clearly present and markedly enhanced relative to the photoluminescence. It is well known that pressure can change both fluorescence and phosphorescence lifetimes in aromatic hydrocarbons.[31] The luminescence quantum yields can also be changed by pressure.[32,33] Emission from traps or defects is likely in the TL experiment as discussed previously. Thus, it is possible that the emitting centers have a larger cross section for excitation by the TL process than by absorption of a photon. Studies are in progress in an attempt to find the solution to the questions raised by these observations.

Tribophosphorescence. Tribophosphorescence is the spin-forbidden luminescence excited by mechanical stress. Only four examples of tribophosphorescence from organic molecular crystals are known: hexaphenylcarbodiphosphorane,[11] and three derivatives of N-substituted anthranilic acids.[8,34] The TL and room-temperature PL spectra of hexaphenylcarbodiphosphorane are superimposed in Figure 4. The luminescence was assigned as a phosphorescence on the

basis of its lifetime of 0.11 ms at 77 K. A recent molecular orbital calculation[35] suggests an n–π* orbital assignment.

Both hexaphenylcarbodiphosphorane and N-acetylanthranilic acid are of additional interest because of a close relationship to nontriboluminescent forms. The former can be crystallized under different conditions to yield both the triboluminescent crystal and a nontriboluminescent form.[36] The TL-active form slowly converts into the TL-inactive form. X-ray crystallographic studies show that the active form consists of rows of molecules, one with P–C–P bond angles of 130° and the other with angles of 144°. The triboluminescent inactive crystal contains only molecules with a P–C–P angle of 132°. The implications of these observations to the mechanism of TL excitation will be discussed later. N-Acetylanthranilic acid is triboluminescent, while its derivatives differing by one CH_n unit, N-formyl- and N-propionylanthranilic acid, are nontriboluminescent.[36] Structural studies on this series are in progress. Both of the series discussed above may provide evidence for structural or packing requirements for TL.

Metal-Centered TL. The TL of many substances has been spectroscopically shown to originate from excited states of metal ions or complexes. The TL of crystals composed of discrete metal complexes is closely related to the TL considered in the previous two sections. In these types of crystals, the emission is also a localized transition, but it involves the d or f orbitals on the metal. Most frequently, these transitions are formally phosphorescences, although the spin label is not as meaningful for heavy metals with large spin–orbit coupling constants. A second common type of metal TL occurs in crystals containing traces of metal ion impurities as the emitting centers. In these cases, energy transfer from the bulk crystal to the emitting metal impurities precedes the metal-centered luminescence. Finally, in the case of NaF, the metal-centered emission occurs from the sodium ion. Each of these categories is considered individually below.

The known examples of TL from discrete metal complexes are tetrahedral manganese(II) complexes,[18,37] uranyl salts,[17] and tetrakis(dibenzoylmethido)europate(III) complexes.[8,19] Spectra of a manganese complex and a uranyl salt are shown in Figure 5. . The manganese complex TL is the $^4T \rightarrow {}^6A$ d–d phosphorescence and the uranyl TL is the $^3\Pi_u \rightarrow {}^1\Sigma_g^+$ phosphorescence. Because of the characteristic colors of the metal luminescences, qualitative assignments can frequently be made on the basis of the visual similarities of the colors of the TL and PL. For example, when Eu was replaced by Tb, the green emission from Tb was observed instead of the red Eu emission.[19]

TL from metal impurities in a crystal has been observed in doped ZnS and fluorite. The spectra of ZnS doped with Cu, Ag, and Mn correspond to the PL spectra with small shifts in the energies of the peak maxima.[23] All of these shifts in the TL spectra are in

(31) Reference 28, pp 123–131.

(32) D. J. Mitchell, G. B. Schuster, and H. G. Drickamer, *J. Am. Chem. Soc.*, **99**, 1145 (1977).

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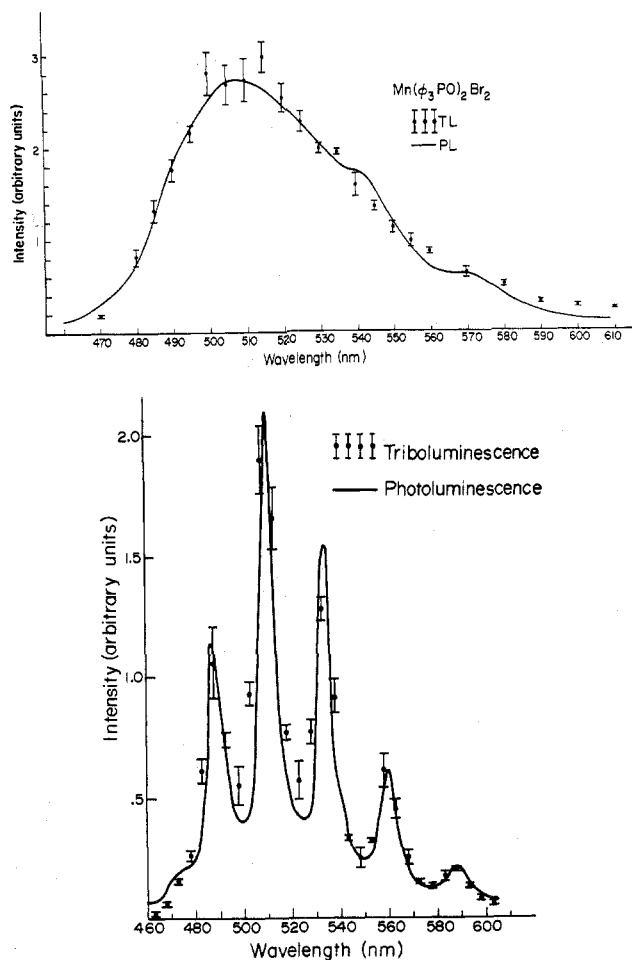
Figure 5. Metal-centered triboluminescence spectra and room-temperature photoluminescence spectra of dibromobis(triphenylphosphine oxide)manganese(II) (top) and uranyl nitrate hexahydrate (bottom).

the same direction as those observed upon application of hydrostatic pressure and correspond to pressures between 2.5 and 3.7 kbar.[23] The spectrum of copper-doped ZnS contains two maxima.[23] The TL spectrum more closely matches the electroluminescence spectrum than the PL spectrum, suggesting that the mechanism of the TL excitation is electrical. Although the mechanistic conclusion has been challenged (vide infra), it is clear that the spectroscopic origin of the TL is the metal impurity. Similarly, the TL spectra of fluorites from different geological sources contained emission bands from rare earth impurities. The bands of Tb and Dy were observed using a visual spectroscope.[21]

The TL spectra of NaF contains a sharp emission line from sodium superimposed on a broad band whose origin is unclear. The latter band will be considered under a separate heading. The sodium emission is unusual and interesting because an energy of at least 1.6×10^4 cm^{-1} must be supplied in order to excite the atom.[23]

Gas TL. The TL of the earliest known triboluminescent crystal, sucrose, had N_2 emission as its origin. The first TL spectrum, also that of sugar, provided clear evidence for N_2 emission.[12] In addition, many workers have inferred the presence of N_2 emission by studying crystals under an atmosphere of Ne and visually observing the characteristic red emission of that gas.[16,38]

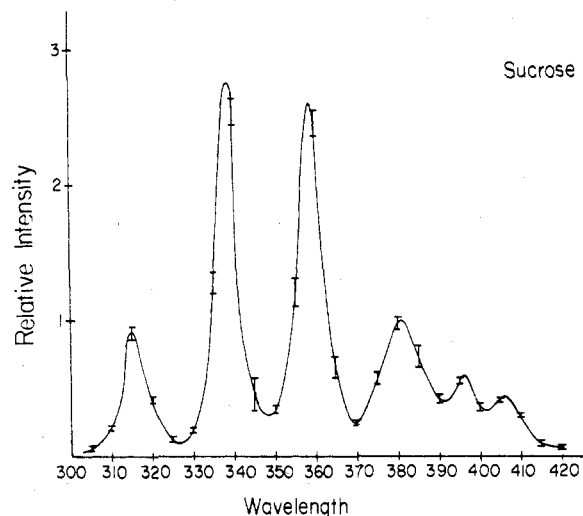(38) E. N. Harvey, *Science*, **89**, 460 (1939).

Figure 6. Triboluminescence spectrum of sucrose, emission from molecular nitrogen.

The nitrogen emission which is observed is the $^3\Pi_u \rightarrow {}^3\Pi_g$ fluorescence with a maximum at 330 nm.[39] A well-defined vibronic band structure is observed, as shown in Figure 6.[15] In order to excite nitrogen to its $^3\Pi_u$ excited state, a minimum energy of 8.9×10^4 cm^{-1} is needed. It is a surprising aspect of TL that energy of the magnitude implied by the nitrogen emission can be generated simply by pressing crystals with a hand-held rod.

Many types of crystals in addition to sucrose are known to produce nitrogen-emission TL. Samples of D-glucose, lactose, maltose, L-rhamnose, and sucrose are triboluminescent, while samples of cellobiose, fructose, fucose, galactose, and mannose are not.[15] Aniline hydrochloride,[14] cis-4-octene,[16] and tartaric acid[13] are other organic crystals in addition to sugars whose sole TL is from N_2. The known examples of inorganic compounds producing N_2 TL are LiF,[24] NaCl,[24] As$_2$O$_3$,[25] and tetrahedral manganese complexes.[18] The latter compounds have the N_2 bands superimposed on the much more intense manganese-centered metal phosphorescence. The arsenic crystals contained the N_2 lines and a broad luminescence which was attributed to arsenic emission.[25] Finally, the TL of cellophane tape (when it is rapidly pulled from a roll),[38] mercury flowing over glass at low pressure,[40] and some candies such as wintergreen lifesavers[41] is primarily N_2 emission. The origin of the TL from the first two was determined by investigating them in an atmosphere of Ne. The spectrum of the latter contains the N_2 line spectrum and the bright luminescence of the flavoring agent, methyl salicylate.

Preliminary experiments have been carried out to determine the location of the emitting nitrogen. A sample of sucrose was vacuum degassed at 80 °C to remove nitrogen adsorbed in the crystals. No TL was observed when this sample was excited under argon stripped benzene. However, TL was observed when the degassed sample was excited in the atmosphere. From these observations, it was concluded that ambient nitrogen gas is not necessary for the phenomenon to

(39) G. Herzberg, "Molecular Spectra and Molecular Structure", Vol. 1, "Spectra of Diatomic Molecules", 2nd ed., Van Nostrand, Princeton, N.J., 1950.

(40) S. De Paoli and O. P. Strausz, *Can. J. Chem.*, **48**, 3756 (1973).

(41) G. E. Hardy, R. Angelos, and J. I. Zink, *J. Chem. Educ.*, in press.

occur, but that adsorbed or absorbed nitrogen is sufficient.[15]

Limited experiments have been performed to determine the role of N_2 emission when two different types of emission occur simultaneously. Because the N_2 emission occurs around 330 nm where many substances absorb, it is possible that any additional luminescence peaks result from absorption of a UV photon from the N_2 TL by the bulk of the crystal followed by crystal fluorescence or phosphorescence. In order to test this possibility, a sample of Mn-$(Ph_3PO)_2Br_2$ was vacuum degassed and the TL spectrum taken under argon.[18] No N_2 emission was observed, although the bright manganese-centered TL remained. For this crystal, the molecular luminescence is not indirectly excited by absorption of a photon from N_2 TL.

TL from Charge-Transfer Complexes. The spectroscopy of organic charge-transfer (donor–acceptor) complexes has been well studied.[42] To date, the only known example of charge-transfer TL is from 1:1 phenanthrene/tetrachlorophthalic anhydride (TCPA).[8] Other photoluminescent charge-transfer complexes studied were 1:1 anthracene/TCPA, 1:1 fluorene/TCPA, 1:1 chrysene/TCPA, and 2:1 chrysene/TCPA. TL was not observed in any of these complexes.[8]

Uncommon Origins of TL. Three origins of TL in addition to those discussed above have been reported. The best characterized of these, emission from small organic radicals produced when solid methanol undergoes the $\beta \rightarrow \alpha$ phase change,[22] is best considered to be an unusual example of chemiluminescence. In all of the other examples discussed above, the TL originated from the original molecules and not from new chemical products. Much more poorly characterized is the broad, featureless emission observed from alkali halides at low ambient gas pressure.[23,24] The broad band was attributed to blackbody radiation by one group[23] and to radiative transitions from the conduction band to surface levels by another group.[24] The correct assignment is uncertain.

Mechanistic and Mechanical Aspects of TL

The mechanisms by which TL is excited are poorly understood. Thus, in contrast to the detailed discussions of excited-state origins and spectral features which are possible because of advances in TL spectroscopy, the discussion of the mechanistic and mechanical aspects of TL will be more general. The purpose of this section is to briefly present the mechanisms currently under consideration and to evaluate them in terms of experimental results.

The three mechanisms of triboexcitation which are currently under active consideration can be broadly categorized as electrical, thermal, and chemical. Each of them consists of a broad range of physical processes. As will be seen, the problem is not one of an absence of mechanisms which can explain the excitation, but rather one of too many viable possibilities.

The electrical mechanisms which have been proposed all require that mechanical energy generates free electrons which leads to emission of a photon by electron impact on molecules, electroluminescence, or recombination of cations and anions. The electrons could be generated by piezoelectric effects caused by compression of noncentrosymmetric crystals, frictional electrification caused by rubbing two dissimilar materials together, or electrification within a crystal caused by shear, cleavage, or rupture of the crystal. The existence of a specific mechanism is difficult to assess because one or several of them could be simultaneously operative.

Piezoelectrification of a crystal by pressure requires that the crystal be noncentrosymmetric.[43] Most of the triboluminescent crystals which have been studied are noncentrosymmetric. For example, of the aromatic crystals which have been studied spectroscopially, the space groups of only eight have been reported, and only one, *p*-anisidine, is centrosymmetric.[8] In this one case, piezoelectrification is not important. No generalizations can yet be made because some TL crystals are centrosymmetric, and not all photoluminescent, noncentrosymmetric crystals are triboluminescent. Some further complications are illustrated by ZnS. Because the TL spectrum matched the electroluminescence spectrum, the mechanism of excitation was proposed to be tribo-induced electroluminescence.[23] To test this explanation, a hydrostatic pressure large enough to produce a piezoelectric polarization higher than that required to excite electroluminescence was applied. No TL was observed.[44] In this example, piezoelectrification large enough to cause TL does occur, but it does not excite TL.

The importance of frictional electrification was probed by grinding the triboluminescent crystals with a variety of materials in a variety of vessels.[8] If frictional electrification were of primary importance, large differences in TL intensity would be expected as the types of materials rubbing together are changed. The observed TL was qualitatively unaffected by the type of implement (conducting, nonconducting). TL can be excited in many crystals by thermal shock caused by immersing them in liquid nitrogen. In this experiment, no grinding implement is used. TL has also been observed by grinding the crystals under liquids in which they are insoluble. In all of these cases, frictional electrification could occur because dissimilar materials are in contact. Because no systematic differences are observed, surface frictional electrification does not appear to be of primary or general importance in exciting TL when crystals are ground. In contrast, the TL caused by the motion of mercury over surfaces is caused by electrification. Potential differences of over 20 V and TL have been recorded.[45]

Internal electrification of a crystal by fracture cannot be tested as easily. This type of electrification is expected to occur when crystals are crushed. It is the most likely mechanism for the excitation of nitrogen gas emission. This mechanism is strongly supported by the observation that electromagnetic radiation (probably caused by accelerating electrons) is detected coincident with the crystal fracture and coincident with the TL of LiF, NaCl,[46] and SiC.[47] Studies of the stress depen-

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dence of TL suggest that TL intensity depends on the area of new surfaces created by fracture.[48-50] However, other workers claim that crack growth and rupture are not required for TL, but that TL can be excited by plastic deformation.[51] In order to disentangle the conflicting mechanisms and verify that a given electrical mechanism is operative, systematic mechanical studies of crystals of known structure with known TL origins are required.

The category of excitation mechanisms which we call "thermal" includes all of the nonelectrical, nonchemical mechanisms which have been proposed. The three different types of mechanisms which have been proposed are excitation by pressure-induced intramolecular distortions, excitation by pressure-induced intermolecular interactions, and excitation by the movement of dislocations. The reason for the general categorization of these mechanisms as thermal will be illustrated in the discussions below.

The first two of the thermal mechanism may be rather closely linked. High-pressure studies have demonstrated that the energy separation between the ground and excited states can change as a function of pressure and that thermal population of a state which is an excited state at atmospheric pressure can occur at high pressure.[52] Upon release of the pressure, emission could occur. The energy changes can be caused by intra- or intermolecular changes. Spectroscopic studies of tetrahedral manganese complexes illustrate both the feasibility and the ambiguity of this mechanism.[18] The photoluminescence spectra were measured at pressures up to 42 kbar. The emission energy decreased linearly with pressure and extrapolated to zero energy at pressures ranging from 500 to 700 kbar. The two most important considerations are whether the extrapolation is a valid method of estimating the pressure at which the excited state is within RT of the ground state, and whether the required pressure can be attained in the TL experiment. The extrapolated pressure is probably an upper limit to the required pressure. Drickamer has shown that the Franck–Condon transition energy between two states observed spectroscopically may generally be much larger than the energy between the potential minima of the states.[52,53] Furthermore, as the effective Dq increases as a result of the pressure increasing the

intermolecular interactions and decreasing the metal–ligand bond distances, a new state ($^2T_2$) will drop lower than the emitting state. These arguments suggest that pressures lower than that extrapolated may be sufficient. The second ambiguity is the unknown pressure in the TL experiment. Although relatively small pressures are applied, stresses may be involved which, when considered over the whole volume of the crystal, may be concentrated at favorable sites.[54] Although the mechanism is feasible, further high-pressure studies are required to assess its validity.

A specific example of an intramolecular distortion mechanism is found in hexaphenylcarbodiphosphorane crystals.[8,36] The triboluminescent crystal contains molecules with bond angles of 140° which are calculated[35] to be 12 kcal/mol higher in energy than the molecules having 130° bond angles in the nontriboluminescent crystal form. If the effect of pressure were to provide a pathway (via cracking or plastic deformations) for the TL crystal to convert to the non-TL form, and if the released energy were entirely converted into photons, then six molecules could release one photon, or 1 mol of crystal could release 10^{23} photons. Although these figures are upper limits because neither the accumulation of the energy at sites nor the luminescence quantum efficiency is expected to be quantitative, the mechanism is plausible. This mechanism is probably not general. A more qualitative analysis was used to eliminate bending as a mechanism for excitation of uranyl nitrate.[17]

The third proposed thermal mechanism, movement of dislocations, could excite molecules in three related ways: by the unpinning of a dislocation from a luminescent center, by the impact of a moving dislocation with a trapped electron, and by the translation of dislocations and vacancies with concomitant excitation of valence electrons.[55] These mechanisms were proposed for alkali halides and for sugar, all of which exhibit nitrogen emission.

The final category of excitation mechanisms is tribo-induced chemiluminescence. Tribochemistry does occur when mercury flows over surfaces,[40] and luminescence from reactive intermediates has been observed during the phase changes of solid methanol[22] and the crystallization of molten acetates.[56] However, the chemiluminescence mechanism does not appear to be as general as the electrical and thermal ones. All of the TL we have spectroscopically studied originates from the original molecule and not from new reaction products.

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