Tribo- and Thermo-Luminescence of Aromatic Aldehydes

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We found that two typical aromatic aldehydes, 2-furaldehyde and benzaldehyde, sometimes exhibit triboluminescence when these fluid materials at room temperature undergo phase transitions from their glassy phase to crystalline phases under a reduced pressure at low temperature, *e. g.*, at 77 K. Several optical features thereof have been reported in the present paper. We also often observed characteristic thermal luminescence for a good few 2-furaldehyde solids which were subjected to large and frequent triboluminescence processes.

Triboluminescence (TL), the emission light caused by the application of mechanical stress to solids or by the sudden force decrease or increase in the fracture region of the force, has been known for many crystals.[1-4] The phenomena, however, generally contain many complex and unknown mechanisms. This is the reason why only a few quantitative investigations from the viewpoint of microscopic molecular science have so far been presented despite many macroscopic and phenomenological reports. Recently we found that several aromatic aldehydes exhibit such TL emissions at low temperature such as 77 and 100 K (and seldom *even at 4.2 K*). Some preliminary results for two typical aldehydes, 2-furaldehyde (FA) and benzaldehyde (BA), will be given.

The two aldehyde substances were purified in similar ways to those reported previously.[5] A simple circuit was used to measure electric current waveforms of the TL discharge. The output signal on a 50 Ω resistor was fed into a Sony-Tectronix type 5904 oscilloscope. The purified sample was crystallized in a pyrex glass cell of about 15 mm in diameter after ordinary freeze-pump-thaw cycles. The bath temperature was generally held at 77 K. The gas phase pressure inside the cell was then kept in the region of 1- 10 torr (1 torr = 133.32 Pa). Without a special external stress, especially FA sometimes indicated sparking TL in the course of cooling to 77 K. An application of heat pulses to the cell in the bath[6] or swift rubbing the well-cooled cell by a gloved palm is very useful for observation of these luminescences. In most cases we employed swift rubbing.

Both aldehydes are fluid materials at room temperature (melting point: -36.5 ℃ for FA and -26 ℃ for BA). Each material gives a somewhat transparent glassy solid when the liquid in the cell is rapidly cooled down to 77 K. When the glassy solid is warmed up gradually from 77 K toward its melting point, crystalline whitening starts clearly from the rim of a pyrex glass cell in which the solid is included. No precise data on their crystalline phases have been reported, to our regret. If a critical sample size exceeds in a given cell, freeze-pump-thaw cycles for the sampling preparation sometimes bring about a cell break, meaning a great voluminous change upon such phase transitions as in methanol.[7]

The TL emission of FA is ordinarily categorized into three or more components: bluish violet and sometimes white emission with a decay constant ranged in 10-100 ns, yellow green strong emission with decay constants of 1-10 μ s and similar yellowish green emission with nonexponential long decays of a 1-10 s depending on how sample crystals are warmed up. The wavelength maximum of such yellowish green emissions are located around 550 nm. Almost all of the observed decay curves for the former two cases are generally analyzable by means of two kinetic constants. These constants are, however, considerably different from TL to TL. This difference is probably attributed to a variety of formation of new fractures in the sample crystal and also to frequent propagation of such crystal fractures. Despite this variety of the decay constants observed, it should be noted that the groupings mentioned above is possible. From analysis of electric current waveforms of the TL discharge , we got similar decay constants to the former two short range lifetimes obtained for analysis of the TL emission.

Similarly, the TL of BA was found to consist of 10-100 ns bluish violet (and sometimes white) emission, 1-10 μ s bluish emission, and 1-10 ms bluish phosphorescence. No substantially long life luminescence was observed, however. As for the both aldehydes, to our knowledge, nobody has succeeded in observing prompt fluorescence emissions by photoexcitation as yet. Even phosphorescence emission has not been detected for FA.

A very characteristic event in the present work is an observation

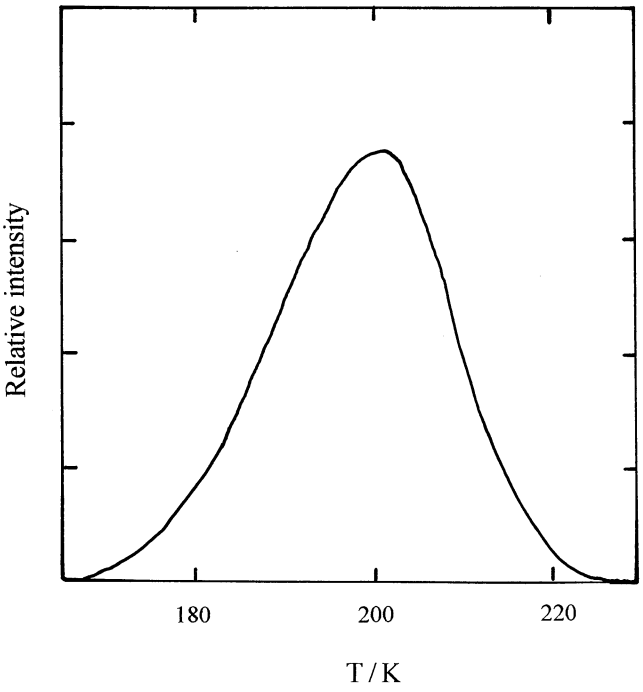

Figure 1. A change in intensity of long-lived luminescence of 10^{-2} mol/dm^3 NMP/FA crystal with an increase in bulk cell temperature. Temperature increase rate employed was about 20 ℃/min in the observed range.

of thermal luminescence (THL) in FA solids. This unusual emission is often observed for pure FA solids or solids containing a small amount of an impurity. One of the most effective impurities is N-methyl-phenothiazine (NMP) which has a low ionization potential.[8] A THL example is shown in Figure 1. Although a peak appears around 200 K, it should be noted that this moves within ± 10 K on going one sample to the other. Further, relative thermal emissions decrease in intensity considerably and the peak is apt to move toward the lower temperatures when slower rates of the temperature increase are employed.

Most probable TL mechanism in FA and BA solids are summarized as follows: (1) local phase transitions in solids followed by crystalline fracture in part; (2) partially created high electric fields on such fracture planes together with plasma emissions; (3) molecular excitation by surface charges and/or space charges together with radical emissions; (4) gas dynamics domain between the surfaces together with atomic and molecular emissions; (5) energy transfer and energy relaxation in solids with phosphorescence (for BA); and recombination process of solvated electron with charged molecules together with characteristic thermal luminescence (for FA).

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