J. Phys. Chem. 1984, 88, 1698–1701

Electron and Positive Ion Emission Accompanying Fracture of Wint-o-green Lifesavers and Single-Crystal Sucrose

J. T. Dickinson,* L. B. Brix, and L. C. Jensen

Department of Physics, Washington State University, Pullman, Washington 99164-2814
(Received: August 1, 1983)

It is a well-known fact that, when Wint-o-green Lifesavers (Lifesaver is a registered trademark of Lifesaver, Inc.) are broken in air, one observes intense triboluminescence. We report here measurements of the emission of electrons and positive ions from the fracture of these Lifesavers under vacuum, as well as from single-crystal sucrose. The emission of photons and radio waves during fracture under vacuum is also presented for sucrose, indicating the occurrence of a gaseous discharge in the crack tip during crack growth. Comparisons of the various emission curves are presented and discussed in terms of stress-induced charge separation.

Introduction

Fractoemission (FE) is the emission of particles, i.e., electrons, ions, neutral species, and photons, during and following the fracture of a material. In recent papers (see ref 1 and the references contained therein) we have shown that fracture under vacuum of a large number of materials where charge separation occurs on the fracture surface leads to intense, long-lasting electron emission (EE) as well as positive ion emission (PIE). We have recently presented a qualitative model[2] for such systems which explains a wide range of observations. In this model, charge separation is accompanied by neutral emission[3] causing a gaseous discharge to occur in the crack tip region. This breakdown results in bombardment of the fracture surfaces by the charged particles produced in the discharge, which leads to eventual electron emission via electron–hole recombination (which can also yield visible photons, i.e., thermoluminescence[10]).

While carrying out studies verifying this model we became interested in systems where fracture produces triboluminesence or fractoluminescence, which has been attributed principally to charge separation,[2] reasoning that there might also be observable EE and PIE from such samples. It is a well-known fact that, when Wint-o-green Lifesavers are fractured in the dark, one can easily observe the accompanying photon emission (phE) with the naked eye. Zink and co-workers[4–7] have attributed this triboluminescence in part to the electrical breakdown of air (N_2) at the crack tip due to the intense E fields caused by charge separation in the sucrose crystals contained in the Wint-o-green Lifesavers. Presumably these charged surfaces are produced by stress-induced polarization of sucrose crystals (a form of piezoelectricity) which, upon fracture, leads to charge separation.

In this work we first asked whether Wint-o-green Lifesavers fractured under vacuum emit electrons and positive ions. Finding this to be the case, we then fractured single-crystal sucrose (the major ingredient in the Lifesavers) and found that it also emitted electrons and positive ions. We then sought evidence of a gaseous discharge occurring during fracture under vacuum, by detection of visible photons (phE) and radio waves (RE), similar to the noise picked up on an AM radio during a lightning storm, but considerably less intense. The results presented here support the concepts suggested in our model[2] and also explain how the fracture of a molecular crystal, which should not yield substantial covalent bond breaking, can lead to energetic processes such as electron and ion emission.

Experimental Section

Single crystals of sucrose were grown by allowing a saturated solution of sugar in water to evaporate. Crystals began forming—usually growing down from the surface—within 1 week and were large enough to use after 2 or 3 weeks. The crystals were then carefully removed from the container and left to dry in air for several days, after which the largest crystals were carefully separated from other crystals by cleavage.

The crystals were then prepared for use in a miniature three-point bending apparatus, which was used to fracture the samples under vacuum. A sample could be cut to the proper size by cleaving a crystal along one of its axes with a sharp blade. Any irregularities or small crystals growing on the larger crystal were removed with an abrasive. Wint-o-green Lifesavers were prepared for breaking by simply cutting small rectangular sections with a jeweler's saw. Typical dimensions for both types of samples were 1 mm × 3 mm × 6 mm.

The three-point bending apparatus held the ends of the sample fixed while applying pressure to the center until fracture occurred. The device was operated from outside the vacuum chamber by means of a bellows arrangement. The experiments were carried out at a pressure of 10^{-5} Pa.

Charged particles were detected with a channel electron multiplier (CEM), Galileo Electro-Optics Model 4039, positioned 1 cm from the sample surface. The front cone of the CEM was biased at +600 V for efficient detection of electrons and at −2500 V for detection of positive ions. The pulses out of the CEM were 10 ns in duration. Following amplification and discrimination, the pulses were counted and stored in a computer-based multichannel analyzer set at 0.8 s/channel.

The photon detector was a Bendix BX754A Photon Counter Tube with an S-20 photosensitive cathode and a background count rate of 10–20 counts per second. The tube was placed under vacuum a few millimeters from the sample looking into the region where fracture would occur. A CEM was placed as close as possible (approximately 5 cm from the sample) to simultaneously detect the charged particle emission.

Results

The single crystals of sucrose tended to have rough fracture surfaces, perhaps due to minor imperfections and impurities in

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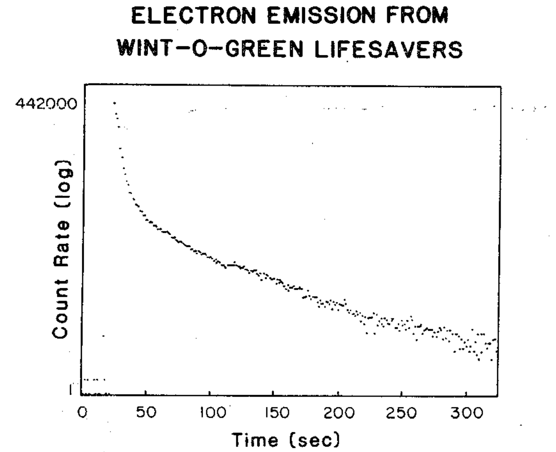

Figure 1. Electron emission (log scale) from the fracture of a Wint-o-green Lifesaver.

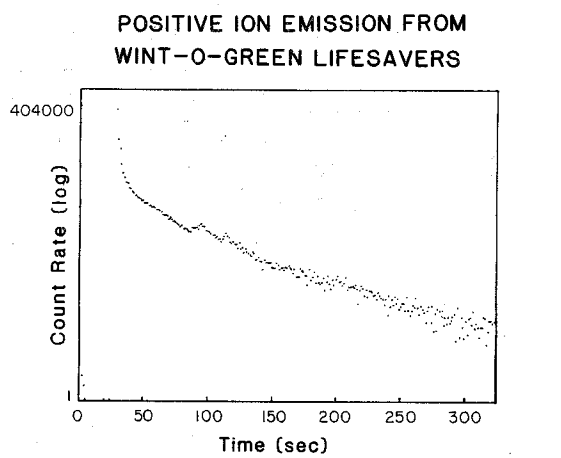

Figure 2. Positive ion emission from the fracture of a Wint-o-green Lifesaver.

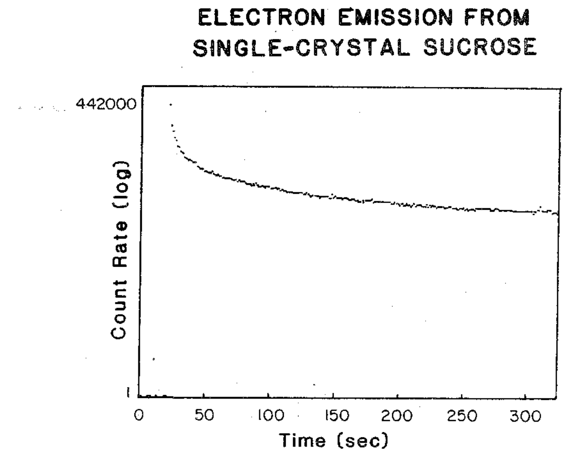

Figure 3. EE from single-crystal sucrose.

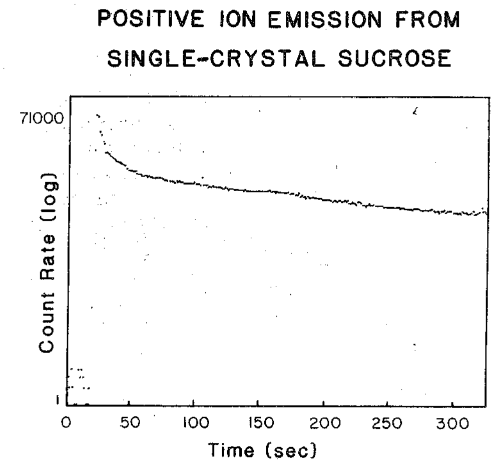

Figure 4. PIE from single-crystal sucrose.

the crystals. Both the sucrose crystals and Lifesaver samples sometimes broke into more than one piece or crumbled into many pieces. Qualitatively, in the case of EE from sucrose, the emission was roughly proportional to the cross-sectional area of the fracture surface.

Wint-o-green Lifesavers emitted both electrons and positive ions during and after fracture. Figure 1 shows typical EE from a Wint-o-green Lifesaver. The PIE for a Wint-o-green Lifesaver is shown in Figure 2 and is seen to follow closely the curve for the Lifesaver EE. We have observed similar behavior of EE and PIE in a number of other materials where charge separation is strong, including SiO_2, lead zirconium titanate, mica, and systems undergoing interfacial failure between polymers and both dielectric and metal substrates. Figure 3 shows the EE from a sucrose crystal. The PIE from sucrose, shown in Figure 4, again has the same general form as the EE.

The decay for sucrose is noticeably slower than that of the Wint-o-green Lifesavers. The peak counts for sucrose and Lifesavers are very nearly the same; the total counts for sucrose are approximately twice those obtained for the Lifesavers due to the longer tail. The total intensities per unit cross-sectional area for both these materials are above average for the wide range of materials that we have examined.[8]

Zink et al. have found that phE (triboluminescence) from Wint-o-green Lifesavers fractured in air appears to occur only during the propagation of the crack. The duration of phE from a single crack should be about the same as the time required for a crack to move through the sample, i.e., on the order of a few microseconds. EE and PIE from the Wint-o-green Lifesavers and sucrose, on the other hand, lasted many seconds, the emission intensity gradually decaying over a period of time. Thus, we see that phE produced in air and the EE and PIE produced under vacuum exhibit completely different behavior.

To compare the charged particle emission with possible phE occurring under vacuum, and to obtain further information on the mechanism, we examined the EE and phE, as well as the accompanying radio-wave emission (RE), from the fracture of single-crystal sucrose under vacuum. The RE was detected with a small pickup coil placed near the sample.[2] As shown in Figure 5, the RE and phE occur only during fracture, while the EE is, as before, most intense during fracture, followed by the usual tail.

For some sucrose samples, the phE was sufficiently intense that we were able to observe a component *after* fracture which showed evidence of decaying in step with the EE. Figure 6 shows phE from two samples, taken on two different time scales: (a) 40 ms/channel and (b) 0.8 s/channel. The second sucrose sample broke into several pieces, thus yielding multiple peaks. In both figures there are clear indications of a phE tail following fracture similar to what we observe in the EE. In Figure 6b, the peak phE (note log scale) is seen to be considerably higher than the remaining emission, with a sharp discontinuity. This suggests different mechanisms for phE during and after fracture.

Discussion

Our data clearly indicate that fracture of Wint-o-green Lifesavers and single-crystal sucrose under vacuum is accompanied by EE and PIE which differ dramatically in form and time dependence from the phE observed in air by Zink and from the vacuum phE data that we have taken. The similarities between the Lifesaver and sucrose EE and PIE suggest that the basic cause of FE from the Lifesavers is fracture of the sucrose crystals contained in the Lifesavers. The faster decays of the Lifesaver EE and PIE may be due to the influence of the flavoring agent (methyl salicylate) on the processes causing postfracture emission.

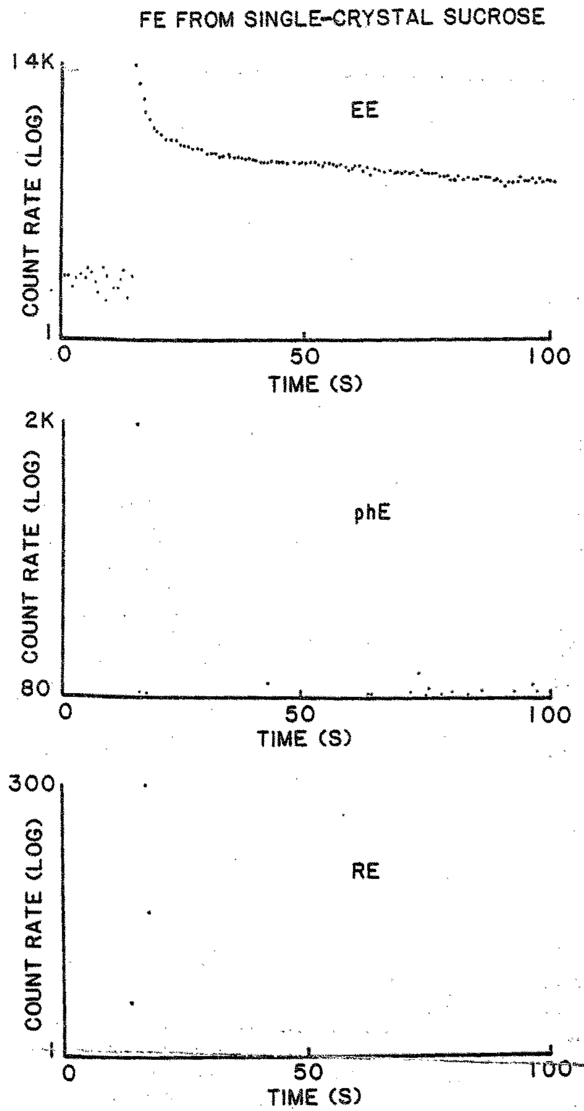

Figure 5. Simultaneous emission of electrons, visible photons, and radio waves from single-crystal sucrose.

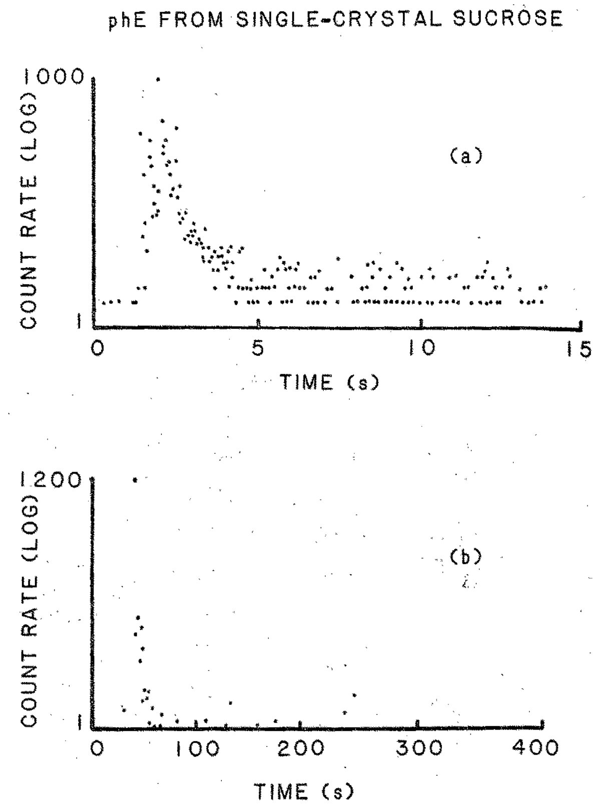

Figure 6. Visible photon emission from fracture of single-crystal sucrose for two samples, taken on different time scales: (a) 40 ms/channel and (b) 0.8 s/channel.

RE has previously been observed by Derjaguin et al.[9] during the peeling of polymer films from dielectric substrates (at much higher pressures than in our experiments) and was attributed to electrical breakdown in the background gases. The RE that we observe is due not to background gases but to gases desorbing from the crack wall into the crack tip. Zink et al.[7] showed that vacuum-degassed sucrose would not produce triboluminescence when the crystals were broken in liquid benzene (free of N_2), which suggests that our undegassed samples may be evolving N_2 during fracture, leading to the discharge.

The detection of RE and the intense phE during fracture of sucrose under vacuum supports our hypothesis of a gaseous discharge, caused by strong charge separation, in the crack tip during fracture. The resulting charged particles in this microdischarge should be strongly attracted to the oppositely charged surfaces, leading to bombardment of these surfaces. As we have shown in ref 2, this bombardment can lead to both EE and PIE. The mechanism for the EE is basically electron–hole recombination[10] where the necessary excitations were originally created by particle bombardment occurring during the discharge. Since trapped electrons must be mobilized in order to locate an appropriate hole, the rate of postfracture EE will depend on electron and hole concentrations as well as the electron-transport process. The phenomenon of radiation-induced electron emission, normally studied in inorganic materials, is called thermally stimulated electron emission.[10] A process parallel to this nonradiative electron emission is the emission of photons (thermoluminescence[10]), which accounts for the tail observed in the phE after fracture under vacuum. This tail may not be observable in the triboluminescence produced in air because of a quenching of the necessary excitations by reactions with air molecules.

The PIE is assumed to be due to self-bombardment, i.e., "self-flagellation", of the fracture surface with electrons which cannot escape due to electric fields from adjacent charge patches. This self-bombardment of the fracture surfaces induces PIE via an electron-stimulated desorption (ESD) mechanism.[11] The PIE rate should then follow the overall EE rate, explaining why we observe identical decay curves for EE and PIE.

In passing we should note that the shape of the EE and PIE curves, in particular the relatively rapid decay that occurs immediately after fracture, may be due in part to the temperature of the fracture surface being elevated by crack propagation and then cooled to room temperature in a few seconds via conduction and radiation. The EE and PIE intensities would follow this decrease in temperature. We are pursuing quantitative models of the kinetics of the EE processes and eventually hope to use the EE to obtain accurate measurements of the temperature rise of the surface produced by fracture.

Conclusions

The phE (triboluminescence) of Wint-o-green Lifesavers and sucrose for fracture in air has been strongly linked to charge separation on the fracture surfaces by Zink and co-workers.[4–7] We have obtained similar results for phE under vacuum for the fracture of single crystals of sucrose. Furthermore, we have shown that EE and PIE also occur under vacuum for both the Lifesavers and sucrose. The similarities of the time decays suggest that EE and PIE from the Lifesavers are due to fracture of the sucrose contained in the Lifesavers. The phE that we observed appears to have two components: (1) photons from a discharge in the crack during fracture and (2) thermoluminescence after fracture. The

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latter is a relaxation process that occurs in parallel with the EE; both are due to electron-hole recombination. Strong evidence for the occurrence of the gaseous breakdown is the RE and the intense component of phE occurring during fracture.

One final result that was not reported above that should be noted is that, after fracture under vacuum, the Wint-o-green Lifesavers tasted rather bland. Although we have not performed the control experiment, we are confident that fracture had nothing to do with the change in flavor. One must ask, in addition, what influence FE might have on the physiological experience of eating Lifesavers.

Acknowledgment. We thank E. E. Donaldson and A. Jahan-Latibari for their contributions to this research and helpful discussions. This work was supported by the Office of Naval Research, Contract N0014-80-C-0213, the National Science Foundation, Grant DMR 8210406, Sandia National Laboratories, NASA—Ames Research Center, and the M. J. Murdock Charitable Trust.

Registry No. Sucrose, 57-50-1.