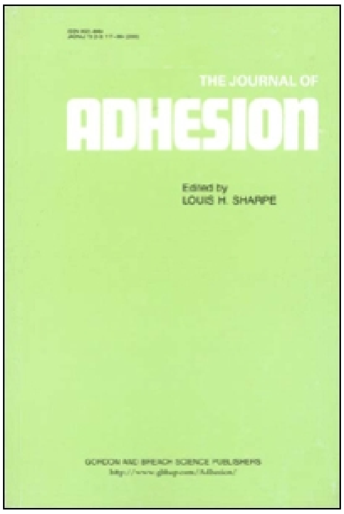

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Zhenyi, Ma , Jiawen, Fan and Dickinson, J. T.(1988) 'Properties of the Photon Emission Accompanying the Peeling of a Pressure-Sensitive Adhesive', The Journal of Adhesion, 25: 1, 63 — 77
To link to this Article: DOI: 10.1080/00218468808075442
URL: http://dx.doi.org/10.1080/00218468808075442

J. Adhesion, 1988, Vol. 25, pp. 63–77
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Printed in the United Kingdom

Properties of the Photon Emission Accompanying the Peeling of a Pressure-Sensitive Adhesive

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(Received July 13, 1987; in final form September 28, 1987)

During the peeling of pressure-sensitive adhesives, it is well known that visible light is emitted from the region near the detachment zone. This photon emission due to adhesive failure is a unique form of *triboluminescence*. In this paper, we further investigate the properties of this light from the peeling of a filament tape with a natural rubber-resin adhesive from its backing at various peel speeds. We show conclusively that small electrostatic discharges are the major source of this radiation. Total intensity *vs* time measurements show that the light consists of very intense bursts with typical duration of 50 ns which frequently induce additional discharges for times as long as 50–100 μs. Time resolved spectra of these emissions show them to be dominated by the line spectrum of molecular nitrogen for both the initial burst and those that follow in the next 0.1–100 μs. Thus, the "after-emission" is not due to phosphorescence of the polymer(s), but due to these additional electrostatic discharges.

KEY WORDS Triboluminescence; fracto-emission; charge separation; microdischarge; optical spectra; time-resolved spectroscopy.

I INTRODUCTION

A number of researchers[1–5] have investigated the well known *triboluminescence* observed during the peeling of adhesives from polymers and other substrates. This photon emission accompanying peeling of pressure-sensitive adhesives and other forms of interfacial failure has been attributed to small gaseous discharges due to the intense charge separation which occurs during the separation between two dissimilar materials such as the adhesive and a substrate.[1-5] One test of these mechanisms which we performed involved peeling metal films from an inorganic insulator (glass) and we found entirely similar behavior.[6]

In previous work we have presented details of the properties of the light as well as of the charged particle emission from systems undergoing adhesive failure.[4-11] In particular, we have presented results showing that the detachment of a commercial brand of filament-reinforced, pressure-sensitive tape from its own backing leads to strong bursts of photon and radiowave emission that were strongly correlated in time[4] and that are highly localized spatially in the vicinity of the peel zone.[5] Furthermore, we showed that the averaged intensity *vs* time behavior of these bursts consisted of a narrow, intense spike on the order of 50 ns in duration followed by a decay lasting typically for 50 to 100 μs. We interpreted the spike (found to be in coincidence with the onset of radio wave emission) to be the light from the discharge. The after-emission (the tail) was attributed to phosphorescence from the discharge activated surface.

Earlier published data on considerably different polymer/substrate combinations (*e.g.*, PVC from glass) taken at low spectral resolution (by use of filters) have been presented by Ohara *et al.*[1] and Klyuev *et al.*[3] Ohara *et al.* observed the most intense emission in the region of the spectrum below 490 nm, consistent with gaseous discharges in air. At low pressures, features ascribable to luminescence of the glass substrate were also observed.

In this paper, we present higher resolution spectral measurements of the photon emission from the peeling of 3M Scotch Filament Tape No. 893 detached from its own backing. We present measurements of the time dependence of this emission, acquired at a faster time scale. In addition, we have obtained time-resolved and time-integrated spectra of this light. We examine the spectrum as a function of time relative to the larger bursts of light over a time range of 100 ns to several tens of microseconds. These results verify that, indeed, the initial bursts are due to the breakdown of air, and show that the after-emission is due to additional, smaller microdischarges *triggered* by the initial burst, rather than phosphorescence from the adhesive/backing polymers. In addition, we have also compared the light emitted from the surface several mm from the crack tip *vs* from the crack tip and see again discharge-like spectra. The origin of this light is shown to be due to "light piping" of emission from the crack tip, along the filaments.

II EXPERIMENT

We selected 3M Scotch Brand Filament Tape as a test material. The adhesive is a natural rubber combined with a tackifying agent which is a hydrocarbon resin appearing to be terpene based. More tackifier is used on the face of the adhesive and less in the saturating layer binding the glass filaments to the backing. The polyester tape backing has been treated with a release coating with a critical surface tension for wetting of approximately 21 dynes/cm. The experimental geometry consisted of a roller arrangment such that pre-made sandwiches of adhesive and backing may be peeled apart continuously in total darkness and in the vicinity of a photomultiplier or spectrometer in a T-Peel fashion. All experiments were performed in air at room temperature. The relative humidity during these tests can have an influence on the intensity of the emission and fell in the range from 25–35%.

In Figure 1 we show a schematic diagram of the system for

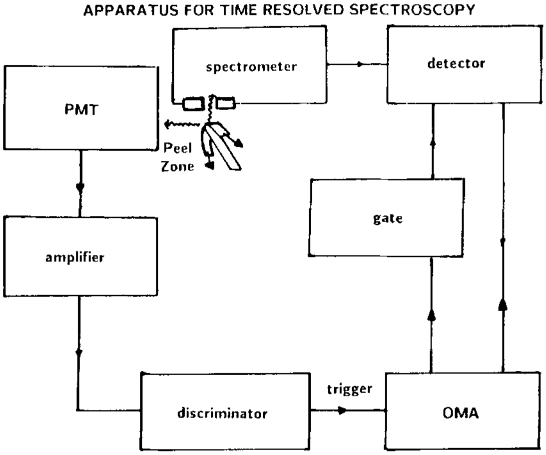

FIGURE 1 Schematic diagram of system for determining spectra of photon emission accompanying adhesive failure.

acquiring spectra of the photon emission accompanying adhesive failure. The detachment zone of the T-Peel was placed approximately 1 cm from the entrance slit of the spectrometer. The crack orientation was at right angles to the slit to minimize stray light in the spectrometer. A 1200 lines/mm grating spectrograph (Thermo Jarrell Ash Monospec-18) was used with a EG&G Model 1421 gatable, intensified position sensitive detector, responsive to light in the region between 200–830 nm. Both time-averaged and time-resolved data were acquired utilizing an EG&G OMA-III system.

A photomultiplier (PMT in Figure 1) located near the peel zone was used to monitor total light intensity *vs* time. With suitable circuitry, burst of light in the peel zone were transformed to 10 ns trigger pulses within a few ns of the onset of the bursts. With a discriminator, large bursts could be easily selected from a distribution of sizes. The spectrometer detector could be gated on at any time relative to this pulse between 70 ns–13 ms and held open for time intervals from 100 ns–10 ms. Time-integrated spectra were acquired for time intervals of approximately 10 s which would correspond to ~5000 bursts. This light thus represented an average of the light emitted before, during and following isolated bursts.

For wavelength calibration we used a commercial mercury lamp whose spectrum contains several shorter wavelength lines in the region of interest.

Figure 2 shows a block diagram of the experimental apparatus for acquiring total intensity *vs* time measurements. In this experiment

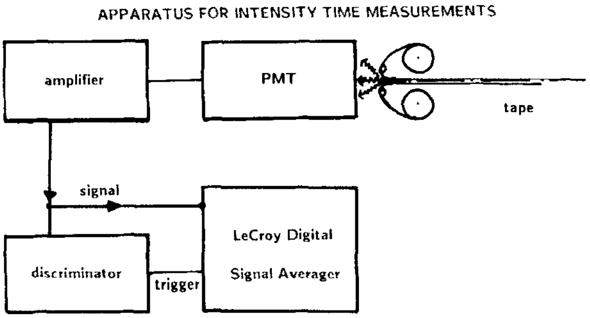

FIGURE 2 Block diagram of experimental apparatus for time *vs* intensity measurements.

the PMT output for a larger burst of photons was treated as a rapidly varying current pulse. After converting this current into a voltage, the resulting signal was amplified by a fast DC amplifier. This amplified signal was then digitized at time intervals of 5 ns/channel. The data were stored in a LeCroy-3500 Data Acquisition System.

III RESULTS

Preliminary studies of time-integrated spectra (over the interval from 200–600 nm) of the visible-near uv light produced during the peeling of 3M Filament Tape from its own backing showed that the emission was all concentrated in the wavelength interval from 300–440 nm. The time integrated spectrum in this region is shown in Figure 3. Since the data were acquired continuously (therefore before, during, and following a large number of bursts), it contains photons produced both during the discharges *and* afterwards. First,

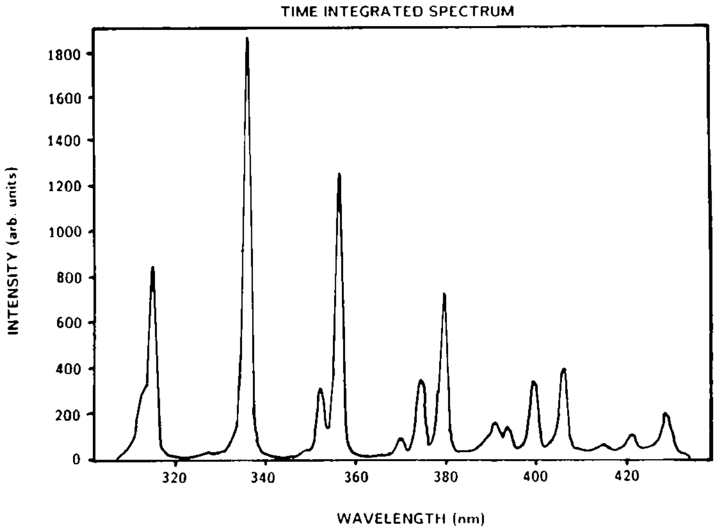

FIGURE 3 Typical spectrum in the region from 300 nm to 440 nm of the photon emission during the peeling of 3M Filament tape. These spectra are not time resolved, so represent an integration over time.

we note that it is a discrete spectrum. When compared with the characteristic gaseous discharge emission of N_2, O_2, CO_2, and other gaseous molecules, we found that each of the lines in the peel-induced spectrum corresponded to N_2 spectral lines. The transitions observed are the strong features of the Triple Headed Band[12] involving the N_2 electronic states: $B\,^3\pi \rightarrow C\,^3\pi$. The individual lines correspond to various vibrational states within each of these electronic levels. The fall off in intensity towards shorter wavelengths seen in several of the spectral lines is due to rotational fine structure.

It should be noted that at our resolution the strong O_2 emission lines in this region of the spectrum overlap with some of the N_2 lines, *e.g.*, at 336.7 nm. However, another strong O_2 emission line at 410 nm was undetectable. Consequently, we can ignore any O_2 contribution to the observed lines, including 336.7 nm.

We emphasize that in no part of the spectrum do we observe any evidence of broadband emission, characteristic of a surface or solid state luminescence process, which as previously mentioned, we had expected.

In an attempt to separate out possible luminescence spectra from the discharge spectra, we acquired time resolved spectra of the light produced *after* the bursts, using the system shown in Figure 1. Four time intervals were investigated:

a) 70 ns to 10 μs,
b) 1 μs to 11 μs,
c) 10 μs to 20 μs, and
d) 50 μs to 60 μs.

Here, the $t = 0$ pulse is within a few ns of the rise of the photons in single bursts. Each spectrum (Figure 4) represents acquisition of 10^4 bursts. Because the light intensity is falling rapidly with time, it was necessary to sacrifice spectral resolution increasing the slit width. Nevertheless, we see that the basic shape of the spectrum does not change. The after-emission has the same basic character of light from a discharge in air as opposed to some form of phosphorescence from the material surfaces.

In order to explain how such discharge-like spectra could occur so long after an initial burst, we examined in more detail the decay of

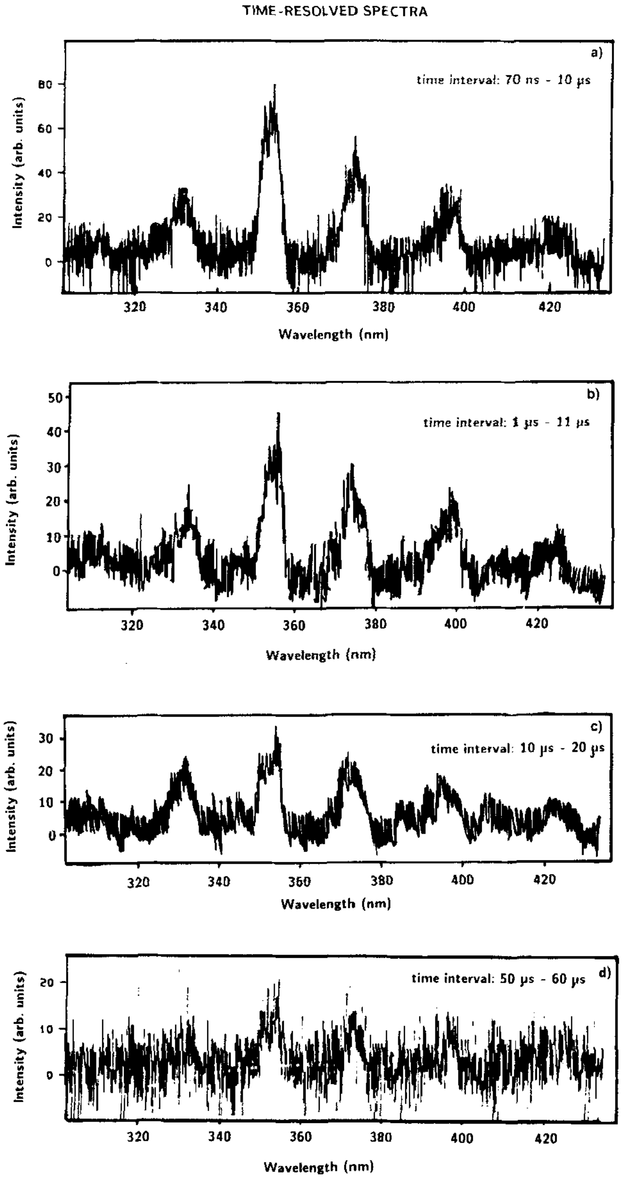

FIGURE 4 Time resolved spectra of the photon emission during different time periods following an initial photon burst.

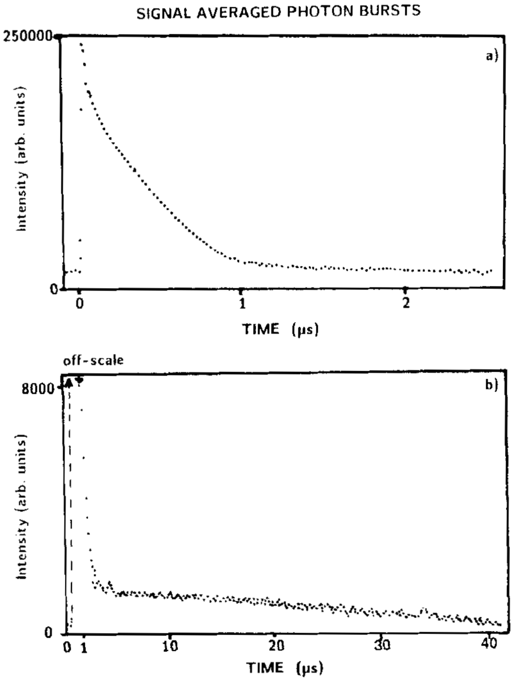

FIGURE 5 The signal averaged intensity *vs* time distribution of the bursts of light during peeling acquired at 5 ns/channel.

the total light intensity following the bursts. Figure 5 shows a signal-averaged intensity *vs* time distribution of the photon bursts as detected by the PMT during peeling. The data were acquired at 5 ns/channel and represent an average over several thousand bursts. Figure 5a are the results showing every channel (*i.e.*, every 5 ns) in the vicinity of the burst; Figure 5b shows the results with data displayed every 0.1 μs. These time-averaged intensities show that the major peak has a feature which lasts less than 50 ns, perhaps limited by the amplifier electronics. This is followed by a second decay with an equivalent time constant of 1 μs. Finally, a third component decays with an equivalent time constant of 20 μs. These results are consistent with earlier pulse counting studies.[4] During all of these regions of time the spectra show discharge character.

Although the decaying emission shown in Figure 5 appears very

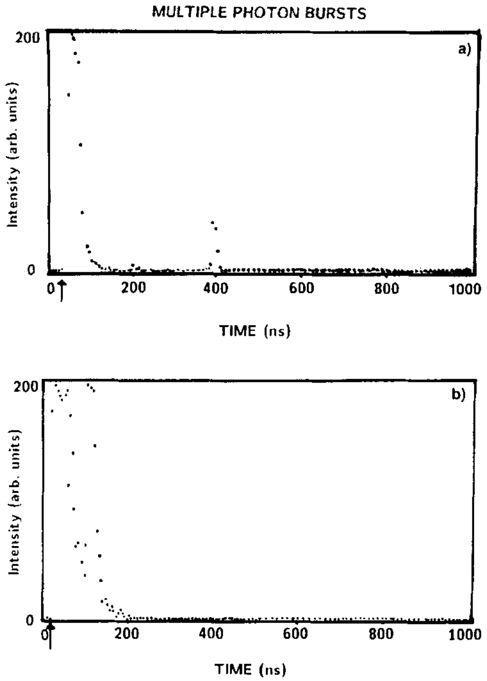

FIGURE 6 Multiple photon bursts which occur during peeling of the tape.

smooth, careful analysis of single bursts show that it is in fact a superposition of many bursts that:

1) occur in a time-correlated fashion with the initial, generally stronger burst, and
2) decay in frequency and intensity as time progresses following the initial burst.

In Figure 6, we show examples of these isolated PhE bursts produced during peeling of the adhesive tape, where the arrows indicate the onset of the initial burst. Both Figure 6a and 6b show two to three bursts occurring on the time scale of a microsecond from *single* initial bursts. Also, viewing a large number of such data, we see no evidence of any smaller precursors to the initial, larger bursts.

If we allow large numbers of these events to accumulate by integrating their intensities by means of signal averaging, they form the smooth curves shown in Figure 5. Thus, the decay constants are really determined by the frequency and size of these "multiple strikes", rather than a solid state relaxation process such as observed in thermally-stimulated luminescence.[13] Instead, it involves a relaxation of surface charge and the interaction of the initial discharge with the charged surfaces and gases nearby.

One other observation that was suggestive of long decay in the light intensity was made by eye. When peeling the adhesive tape in the dark, one could clearly see light coming from the freshly detached surfaces, particularly on the adhesive side, for as far as 1–2 cm away from the crack. Could we be missing a long lasting phosphorescence? By use of proper baffles we could allow this light to enter the spectrometer and exclude the light from the crack. The resulting spectrum is shown in Figure 7. Again, a discharge-like spectrum was observed with slight changes in the relative intensities (*e.g.*, Fig. 3). Examination of the light propagating properties of

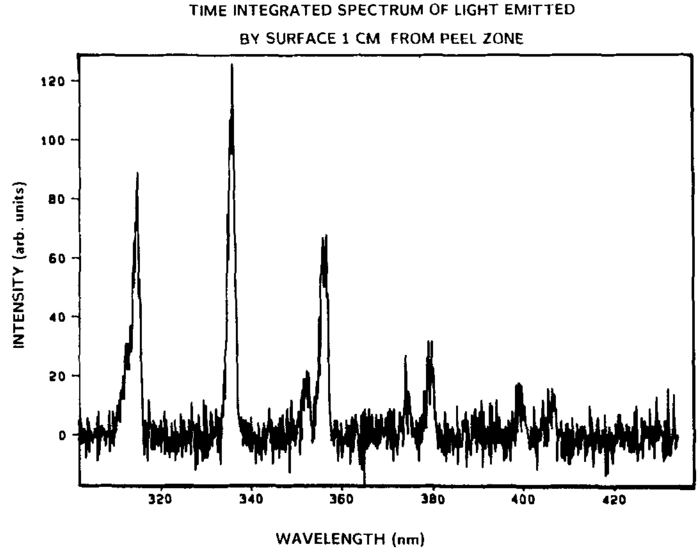

FIGURE 7 Time averaged spectrum of photon emission emanating from the tape surface approximately 1 cm from the peel zone.

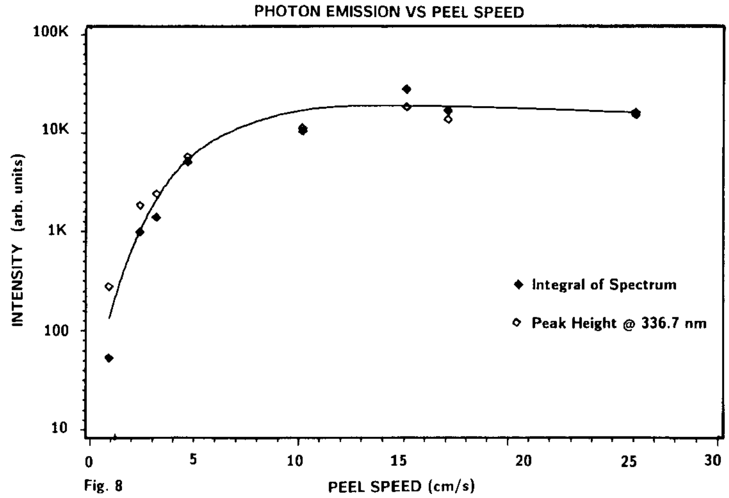

FIGURE 8 Dependence on peeling speed of the integrated intensity of the total photon emission (◆) and intensity of the 336.7 nm spectral line (◇). The two data sets have been normalized to show their similarity.

the tape showed us that indeed photons could be transmitted from the crack tip region, most likely down the strands of glass reinforcing fibers, and be scattered out to the observer, normal to the tape surface. The changes in relative spectral line intensities can be attributed to the "filtering", *i.e,* the selective absorption of the light, which might occur in passing through the fibers and adhesive, apparently favoring the more violet part of the spectrum. So again, there is no evidence of long delayed emission after fracture and the light observed away from the crack is an artifact due to the "light piping" ability of this particular adhesive tape *via* the filaments it contains.

As we have reported earlier, the total photon emission intensities depend on peel speed.[8] In Figure 8 we show on a log scale the dependence on the peel speed of the integrated emission intensity between the wavelengths 300 nm–440 nm (◆) and the intensity of a single N_2 discharge spectral line at 336.7 nm (◇), where we have normalized the data at a single point [26 cm/s]. The behavior is essentially the same in both curves, namely a rapid increase in intensity (nearly exponential) followed by a "saturation" at a peel speed of ~10 cm/s with evidence of a slight decrease at the highest speeds.

In examining the relative spectral intensities of two lines taken at different peel speeds, we find that the ratio of the peaks at 316 and 335 nm changes, namely the ratio I_{316}/I_{335} decreases with peel speed. These lines correspond to transitions involving two vibrational states, namely $v = 1$ and $v = 0$, and to a first approximation, this ratio represents the relative population of these two vibrational levels. Letting n_1 and n_0 represent the respective populations, we have:

$$I_{316}/I_{335} = n_1/n_0 = \exp[-\{E_1 - E_0\}/kT]$$

where E_1 and E_0 are the known vibrational energies of N_2 for $v = 1$ and $v = 0$. From the measured line intensities we can therefore calculate an average temperature in the discharges during peeling. Taking two extreme values in peel speed we calculate the following temperatures for the "sparks" created during peeling:

slow (0.7 cm/s)	4200 K
fast (15 cm/s)	3300 K

Thus, at these particular peeling speeds, the slower peel yields "hotter" discharge events. These different temperatures suggest that discharge conditions in terms of charge separation and gas composition in the crack tip are more favorable at the lower speed for the production of higher energy breakdown events. As a consequence, the gases in the "arc" reach higher temperatures at the lower peel speed. Thus, the much lower overall intensity at the lower peel speed (Figure 8) is due to a much smaller number of discharge events per unit length of peel.

If we hold the peel speed constant but vary the water content of the air by artificially introducing water vapor in the region of the peel, we note that the intensity of the emission drops considerably. This so-called "wet" condition corresponded to 80% relative humidity. If we compare spectra for this "wet" condition with the "dry" condition (slightly different conditions than above), the ratio I_{316}/I_{335} decreases when the water content of the air is higher. For a peel speed of 2.7 cm/s, the calculated spark temperatures were:

a) WET	3900 K
b) DRY	5100 K,

thus showing that the higher humidity reduces the effective strength of the discharges occurring in the peel zone.

IV DISCUSSION

From the experimental phenomena we observed, we conclude that the photon emission is produced by excited electronic transitions in gaseous N_2. The discharge responsible for this excitation initiates because of intense electric fields created by the charge separation as the rubber adhesive detaches from the release-coated polyester backing. The breakdown of the gas takes place when the strength of the electric field attains a critical value for the particular gases in the crack tip.

Immediately following the discharge event, secondary "strikes" can occur in the vicinity of the initial discharge. Electrons or ions created in the first discharge move in a diffusion manner under the influence of the electric field and create secondary charge *via* collisions with gas molecules and surfaces.

The drift velocity in air at atmospheric pressure can be estimated and therefore the distance the charge might travel before a second "strike" might occur. Experimentally derived curves are used[14] which depend on the electric field strength, gas pressure, and temperature. Assuming an electric field strength of 20,000 V/cm (the breakdown potential of dry air), a temperature of 293 K, and a pressure of 760 torr, we determine the following drift velocities in air and the distances the particles move in various times following the initial breakdown event:

Particle	Drift velocity	Dis. in 100 ns	Dis. in 50 μs
electrons	8×10^6 cm/s	8.0 mm	40 cm
N_2^+	3×10^4 cm/s	0.03 mm	1.5 cm
O^-	1×10^5 cm/s	0.1 mm	5.0 cm

At atmospheric pressure, the ionic states are extremely probable, so that the distances we expect the charges to move are on the order of a cm or less. The crack only moves about 0.003 mm in a 50 μs time period, so that it is not likely that the induced arcs are in the direction of the peel zone. More likely are regions *along the peel zone*. Since the tape is 2 cm in width, this sets an upper limit of about 100 μs for the time secondary "strikes" may occur. This is consistent with the duration of the tail observed following the initial bursts. On a much larger scale, lightning bolts in the atmosphere often occur in a correlated fashion, perhaps for similar reasons.

V CONCLUSIONS

In this paper we have presented further details of the photon emission accompanying peeling of an adhesive from a polymeric substrate. A consistent interpretation of these and earlier observations requires that all of the light is due to electrostatic discharges alone. In this particular adhesive-substrate combination, no evidence of an "after-glow", *i.e.*, phosphorescence, involving excitations of the adhesive/backing surfaces was detected. Instead, the decaying light observed following the large bursts consists of a set of correlated bursts, generally of smaller intensity and less frequent occurrence over a time period of 50–100 μs. We have argued that the charge released by the initial discharge drifts to other regions of the crack and initiates the observed secondary "strikes". Since the micromechanics of detachment are very likely critical to the charge separation occurring, varying the rheology either chemically or by temperature variations would be an important direction to pursue.

Acknowledgments

This work was supported by the National Science Foundation DMR 8601281, The Office of Naval Research N00014-18-C-0213, McDonnell Douglas Independent Research Fund, and the Washington Technology Center.

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