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- Cyclic voltammetric experiments on Fe(TFPPBr₉)Cl and Fe(TFPP)Cl were done at 25°C under argon in CH₂Cl₂ with 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. Potentials were versus AgCl/Ag in 1 M KCl. The Fe^{III/II} couple of ferrocene was observed at 0.45 V under these experimental conditions. The Fe^{III/II} potential of Fe(TFPPBr₉)Cl is reversible when excess PF₆⁻ is present. Given the similarity between these halogenated porphyrins and the chlorinated analog Fe(TPPCl₉)Cl [T. Wijesekera *et al.*, *Angew. Chem.* **29**, 1028 (1990)], it is likely that the chloride remains bound or that the chloride dissociation equilibrium is faster than the rate of reduction-oxidation. The Fe^{III/II} potential of Fe(TFPPBr₉)Cl is considerably more positive than those of Fe(TFPP)Cl (-0.08 V) and Fe(TPP)Cl (-0.29 V) [L. A. Bottomley and K. M. Kadish, *Inorg. Chem.* **20**, 1348 (1981)]. Ring-centered oxidation of Fe(TFPPBr₉)Cl was not observed within the solvent limit (~1.8 V), whereas oxidations of Fe(TFPP)Cl and Fe(TPP)Cl were at 1.50 and 1.30 V.
- Hydroxylation of alkanes by Fe(TFPPCl₉)Cl/PhIO [J. F. Bartoli, O. Brigaud, P. Battioni, D. Mansuy, *J. Chem. Soc. Chem. Commun.* **1991**, 440 (1991); D. Mansuy, *Chem. Rev.* **125**, 129 (1993)] and Fe(TFPP)Cl/PhIO [M. J. Nappy and C. A. Tolman, *Inorg. Chem.* **24**, 4711 (1985)] has been reported.
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- Molecular models are based on the x-ray crystal coordinates of Fe(TFPPBr₉)Cl (H. B. Gray *et al.*, in preparation) and TBHP. The extent of saddle distortion in Fe(TFPPBr₉)Cl is of the same magnitude observed in Ni(TFPPBr₉) [D. Mandon *et al.*, *Inorg. Chem.* **31**, 2044 (1992)]; in Cu(TFPPBr₉) and Ni(TFPPBr₉) [W. P. Schaefer *et al.*, *Acta Crystallogr.* **49**, 1743 (1993)]; in Cu(TFPPCl₉) (W. P. Schaefer *et al.*, *ibid.*, p. 1342); in Zn(TFPPBr₉) (R. E. Marsh *et al.*, *ibid.*, p. 1339); and in Zn(TPP(CH₃)₉) [K. M. Barkigia *et al.*, *J. Am. Chem. Soc.* **112**, 8851 (1990)].
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- Molecular models are based on the x-ray crystal coordinates of Fe(TFPPBr₉)Cl (H. B. Gray *et al.*, in preparation) and Fe(TFPP)-O-Fe(TFPP) [A. Gold, K. Jayaraj, P. Doppelt, J. Fischer, R. Weiss, *Inorg. Chim. Acta* **150**, 177 (1988)]. Molecular models of Fe^{III}(TFPPBr₉)-O-Fe^{III}(TFPPBr₉) show severe steric clash between adjacent porphyrin bromine-bromine and bromine-fluorine atoms in eclipsed (along the Fe-O-Fe axis) and staggered structures, respectively.
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Discovery of Intense Gamma-Ray Flashes of Atmospheric Origin

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Detectors aboard the Compton Gamma Ray Observatory have observed an unexplained terrestrial phenomenon: brief, intense flashes of gamma rays. These flashes must originate in the atmosphere at altitudes above at least 30 kilometers in order to escape atmospheric absorption and reach the orbiting detectors. At least a dozen such events have been detected over the past 2 years. The photon spectra from the events are very hard (peaking in the high-energy portion of the spectrum) and are consistent with bremsstrahlung emission from energetic (million-electron volt) electrons. The most likely origin of these high-energy electrons, although speculative at this time, is a rare type of high-altitude electrical discharge above thunderstorm regions.

We report here the detection of high-energy photons from the Earth's upper atmosphere, observed with the multiple detectors of the Burst and Transient Source Experiment (BATSE) (1) on the Compton Gamma Ray Observatory (CGRO). The

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apparent correlation of the events with storm systems leads us to hypothesize that they are caused by electrical discharges to the stratosphere or ionosphere. Runaway discharges to the ionosphere have been predicted (2, 3) and modeled in detail previously (4). These gamma-ray events may also be related to recently recorded optical discharge phenomena above thunderstorms (5, 6) and to other cloud-to-stratosphere discharges that have been reported in the past (7, 8).

The Compton Observatory was launched in April 1991 to perform observations of celestial gamma-ray sources. The BATSE experiment is one of four experiments on the observatory. It serves as an all-sky monitor

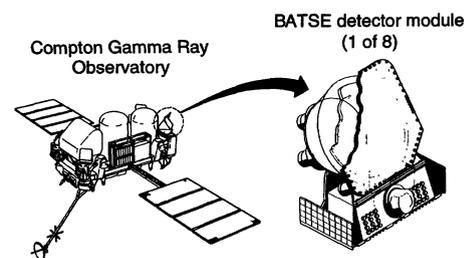


Fig. 1. The Compton Gamma Ray Observatory (CGRO). The eight BATSE detectors, with a sensitive area of about 2000 cm² each, are located on the corners of the observatory.

and has detected over 900 cosmic gamma-ray bursts, several hard x-ray transients, numerous persistent and pulsed hard x-ray sources, and several thousand solar flares. In addition, on rare occasions BATSE has recorded gamma-ray flashes from the Earth. These events have not been reported previously because it was unclear that they were real (noninstrumental) events and that they formed a distinct subclass of BATSE triggered events.

The BATSE instrument consists of an array of eight detector modules located at the corners of the observatory, arranged to provide maximum unobstructed sky coverage (Fig. 1). The scintillation detectors are sensitive to photons with energies above 20 keV. The geometry of the array ensures that sources are usually observed by four detectors. Data from the detectors are processed onboard into several data types with different temporal and spectral resolutions (1). The gamma-ray flashes reported here triggered an onboard burst data recording mode, allowing observations with high time resolution in most instances. Sources are located by comparing the relative responses of the detectors, which view different directions (9, 10).

Two features of these terrestrial events that stand out are their extremely hard spectra and their short duration. They are different from other events that have triggered the detectors, such as gamma-ray bursts, solar flares, fluctuations of other known hard x-ray and gamma-ray sources, and bremsstrahlung radiation from precipitating magnetospheric electrons. Furthermore, these events are located by the BATSE detectors as emanating from below the local horizon. The events that trigger the BATSE detectors are relatively rare, occurring less than once every 2 months. It is likely that many other weaker events of similar origin go undetected because of the trigger criteria implemented by the experiment (1, 9). Because the minimum sampling time for the triggering of the BATSE burst mode is 64 ms, the shortest of these events must be at least ~40 standard deviations above the background rate in at least two detectors to trigger the onboard system.

It is believed that prior instrumentation

Table 1. A list of the 12 events described in this report and shown in Figs. 2 and 3. The geocenter angle is measured from the nadir (the Earth's horizon, as viewed from the spacecraft, is about 70° from the nadir). The location given is that of the spacecraft at the time of the event, not necessarily the location of the origin of the event.

BATSE trigger number	Date	Universal time (s)	Geocenter angle (degrees)	Spacecraft location	
				Lat (N) (degrees)	Long (E) (degrees)
106	22 Apr 1991	02533	35	6	75
868	5 Oct 1991	12711	54	8	359
1433	24 Feb 1992	36549	39	-16	39
1457	1 Mar 1992	81252	46	-7	296
2144	24 Jan 1993	54533	45	6	79
2185	11 Feb 1993	53095	73	-5	119
2223	6 Mar 1993	52583	44	3	115
2348	20 May 1993	07337	59	11	254
2370	3 Jun 1993	14440	25	18	125
2457	23 Jul 1993	18386	15	28	110
2465	26 Jul 1993	16888	39	26	112
2573	9 Oct 1993	38648	31	-24	238

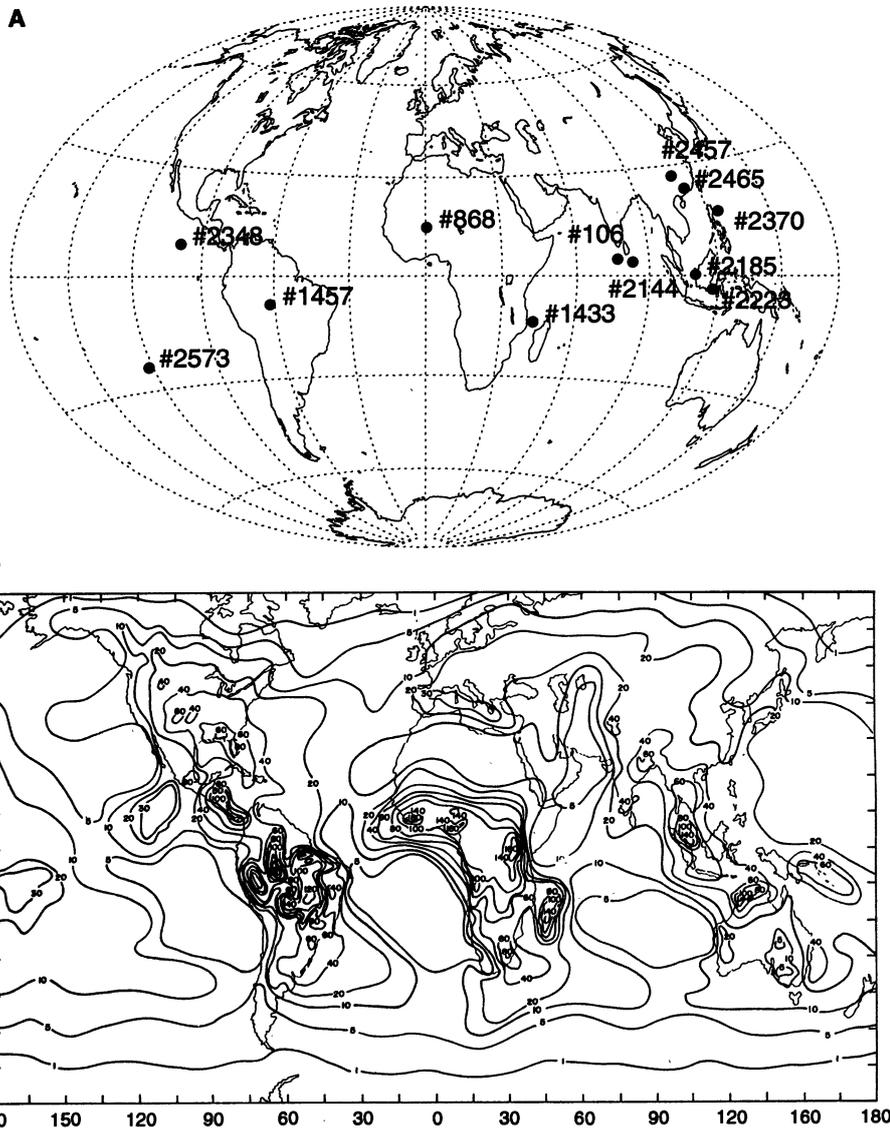


Fig. 2. (A) The approximate locations of the events of Table 1 over the Earth. (B) Contour map of the yearly thunderstorm activity over the Earth (12). Most of the events occurred over regions that have high thunderstorm activity. The spacecraft is limited by its orbital inclination to latitudes within 28.5° of the equator.

and experiments were incapable of detecting this phenomenon for several reasons or that these events may have been overlooked as being spurious. Additionally, most detectors used in high-energy astronomy are collimated and would likely have missed these rare events and data recorded during Earth-viewing times may not have been analyzed. Also, the temporal resolution of most experiments would not have been able to respond to these very brief events or would have had poor signal-to-noise ratios when sampled with coarser time resolution.

The BATSE array of multiple, independent detectors viewing different directions gives us confidence in the reality of these events as opposed to some instrumental or spacecraft effect such as electronic noise. The multiple, wide-field detectors also allow a direction determination to be made for each event (9). The observed counting rate ratios of the detectors are consistent with the source of these events originating from a large distance relative to the spacecraft dimensions. BATSE also contains plastic scintillation detectors that are sensitive to charged particles above ~500 keV. There were no detectable increases in the rates from the charged particle detectors accompanying these events. Finally, independent detectors on another experiment aboard the CGRO [the Oriented Scintillation Spectrometer Experiment (OSSE)] confirm these gamma-ray events (11).

Although the typical BATSE location accuracy for strong cosmic gamma-ray bursts is ~3°, it is estimated that the location accuracy of the events described here is perhaps not better than 10° to 20°. This is attributable to several causes, among them being the limited counting statistics in the detectors and the hard spectra, which lead to increased scattering and transmission through the back of the detectors. Also, the angular extent of the emission is not well determined from these observations alone. The resulting angular uncertainty implies a positional uncertainty from a few hundred to perhaps a thousand kilometers, depending primarily on the observed geocenter angle (the angle from the nadir).

Table 1 lists the data relevant to 12 events recorded between April 1991 and October 1993. Figure 2 shows the spacecraft location at the time of all 12 of the events along with a contour map of the average annual thunderstorm activity over the world (12). The correlation of these two phenomena is quite evident.

We obtained concurrent weather images for seven of the events, two of which are shown in Fig. 3. In each case, storm complexes with well-defined, extensive cloud shields characteristic of thunderstorms are observed. In one case, BATSE event 2348, independent confirmation of lightning ac-

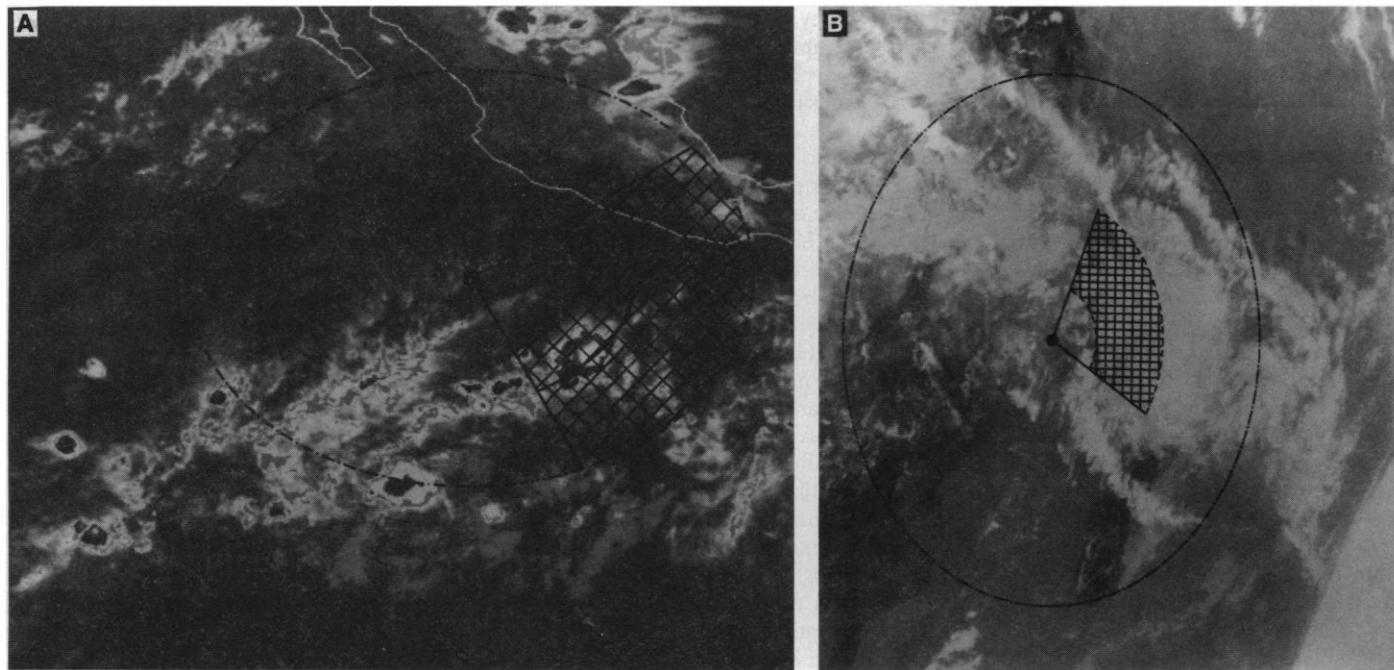


Fig. 3. Cloud images associated with BATSE events (**A**) 2348 and (**B**) 1433. (A) GOES-7 infrared image (enhanced) taken on 20 May 1993 at 0201 UTC, resampled to a spatial resolution of 8 km. The storm is located in the intertropical convergence zone at $10^{\circ}44'N$, $101^{\circ}47'W$, southeast of the CGRO position. The horizontal extent of the nearly circular cold cloud shield at the tropopause is nearly 200 km. The cloud has a minimum cloud top blackbody temperature of 193 K, which corresponds to a height of about 18 km. Between 0200 and 0206 UTC, the U.S. National Lightning Detection Network observed 11 cloud-to-ground lightning discharges in the vicinity of

the storm. (B) METEOSAT 3 infrared image taken on 24 February 1992 at 0955 UTC. A large cyclone with a cloud shield extent of hundreds of kilometers is located to the east of the CGRO position between Madagascar and the African continent. METEOSAT image supplied by the European Space Agency. Superimposed on these images are markings related to the BATSE observations. The subspacecraft point is indicated by the solid dot. The oval represents the approximate horizon of the Earth from the altitude of the spacecraft. The cross-hatched sector is the approximate region from which the event originated, as determined by the BATSE detectors.

tivity was provided by the U.S. National Lightning Detection Network. The probability of detection of these gamma-ray bursts is very small indeed because it is estimated that $<5\%$ of the Earth's surface area in the latitude belt $28.5^{\circ}N$ to $28.5^{\circ}S$ is occupied by thunderstorms at any instant. The instantaneous area on the Earth observable by the spacecraft is $\sim 10^7$ km² (over a horizontal extent of 3000 km).

The BATSE data type with high time resolution used to study the gamma-ray flashes reported here is time-tagged event (TTE) data. These data are recorded whenever the onboard trigger system is enabled. However, sometimes these data are overwritten or otherwise unavailable because of telemetry gaps. In these cases, only data with 64-ms time resolution are available. The TTE data consist of up to 32,000 individual scintillation detector events that are identified by the detector module that recorded it, the energy channel (one of four channels), and the arrival time recorded with a resolution of 2 μ s (relative timing accuracy). The four energy channels cover the following approximate energy ranges: 20 to 50 keV, 50 to 100 keV, 100 to 300 keV, and >300 keV. A continuously operating digital ring buffer allows the recording of about 8000 events before the time of the

trigger recognition. These pretrigger data have been essential in our studies of phenomena with short time scales, such as these events. The time profiles of these events (Fig. 4) consist almost entirely of pretrigger data. Five of the events consist of two closely spaced pulses, from 1 to 4 ms, and one event has at least four distinct pulses of similar shape but variable spacing. The estimated typical gamma-ray energy fluence of these events is on the order of $\sim 10^8$ to 10^9 ergs, assuming isotropic emission and a typical distance to the source of the event of 500 km.

The spectral information that is available from these events is limited because only the four coarse energy channels are recorded in these short time intervals. Hardness ratios (HR) of different combinations of two of the photon counts in two energy channels have been useful in study of the gross spectral characteristics of cosmic gamma-ray bursts and soft gamma repeaters (13, 14). The hardness ratio of channel 3 to channel 2 (HR 3/2) for these terrestrial events is about 2.0 times that measured for the average gamma-ray burst and 1.4 times the value of a subset of gamma-ray bursts with particularly hard spectra. The values for HR 4/1 show an even greater separation between the two

types of phenomena. However, the HR 4/1 parameter has a high statistical uncertainty in many cases because of the limited counts observed in one or both of those two channels. The measured hardness ratios of these events are also considerably higher than those measured by BATSE from any other cosmic sources, such as the Crab Nebula, or from bremsstrahlung produced by precipitating electrons from the Earth's magnetosphere. A model-dependent spectral deconvolution of BATSE four-channel data has also been developed (15). It is found that a bremsstrahlung spectrum with a characteristic energy of 1 MeV is consistent with the observed hardness ratios of most of these events.

In addition to the events listed in Table 1, there were at least five other triggered events during the same time interval (30 months) that are suspected to be of this same type. However, data with high time resolution were not available for these events, preventing us from identifying their nature. Also, there were three other triggered events that had considerably longer duration or for which it could not be well determined that they originated from the Earth-facing direction. Because it is not certain that they are in this same category of events, they have not been included in Table 1. Thus, the total event count in this

time interval is between ~ 12 and 20.

The possibility of strong electric fields producing ionization at altitudes high above the tops of thunderstorms was first discussed about 70 years ago (2, 3); it was recognized that the sudden, strong changes in the thunderstorm electric field caused by lightning discharges might be capable of producing ionization in the upper atmosphere. If the fields were intense enough over a large area, they would be capable of not only ionizing the atmosphere but of producing "runaway" electrons and subsequent bremsstrahlung x-rays. The key to the occurrence of this phenomenon is that the electric field attributable to lightning falls off less rapidly with height above the cloud than does the atmospheric density, which determines the breakdown potential of the air. This might occur, for instance, if the electric field strength at 60 km altitude were to exceed about 500 V/m. Simple electrostatic calculations predict field changes on this order whenever the lightning charge transferred in the cloud is on the order of 300 C. This is a very large charge, but it has been observed in intense storm systems (16).

A field of 500 V/m would have to accelerate electrons over a distance of several kilometers to achieve the megaelectron volt electrons necessary to produce the observed gamma-ray events. The glow-like discharges that have recently been observed optically from aircraft and from the ground (5-7) appear to occur over heights between 40 and

80 km. They extend well over 10 km vertically and from 10 to 50 km in horizontal extent. These events seem to occur over large, horizontally extended storm systems that may be capable of producing the large electric field changes required to directly ionize the atmosphere and, perhaps, produce high-energy electrons.

At least 18 upward-going lightning events have been recorded by video cameras from the space shuttle (6, 17). A number of these events seemed to be quite intense. Some appeared to be connected to the parent cloud; others show no visible connection. All of the events appeared to have horizontal and vertical extents in excess of 10 km. In addition to these well-documented observations, there have been numerous reports by aircraft pilots of upward discharges to the atmosphere, but these have not been treated in the scientific literature (8). It should be noted that x-rays produced in thunderstorms have been measured on various occasions (18), although these measurements were made inside the storms at low (tropospheric) altitudes. These x-rays have also been explained by bremsstrahlung from accelerated megaelectron volt electrons (19).

Numerous observations of lightning discharges have been made from high-flying aircraft (20). The time scales of these optical signatures and electric field disturbances are of the same order as that of the events observed in the present work (~ 0.5 to 1 ms). Thus, an impulsive, high-energy dis-

charge of limited extent seems to be implicated. Any widespread discharge (over 100 km) would not be compatible with the observations, considering the photon travel time and the extensive gamma-ray scattering that occurs within the atmosphere. Observations of short cosmic gamma-ray bursts by BATSE have shown substantial (millisecond) time delay attributable to atmospheric scattering (21).

We have found no prior references to gamma radiation from atmospheric electrical discharges (or from electrons in the magnetosphere) in the literature. Because of the unique nature of these events, the lack of correlated observations in other spectral regions, and the paucity of concurrent weather data, the exact cause of the phenomenon must await further study. Although a detailed cause of these events is lacking, we are convinced of the reality of the observations because of our experience with the instrumentation accumulated over the past 2+ years of operation in orbit, along with the extensive observations of a wide variety of celestial sources with the same experiment.

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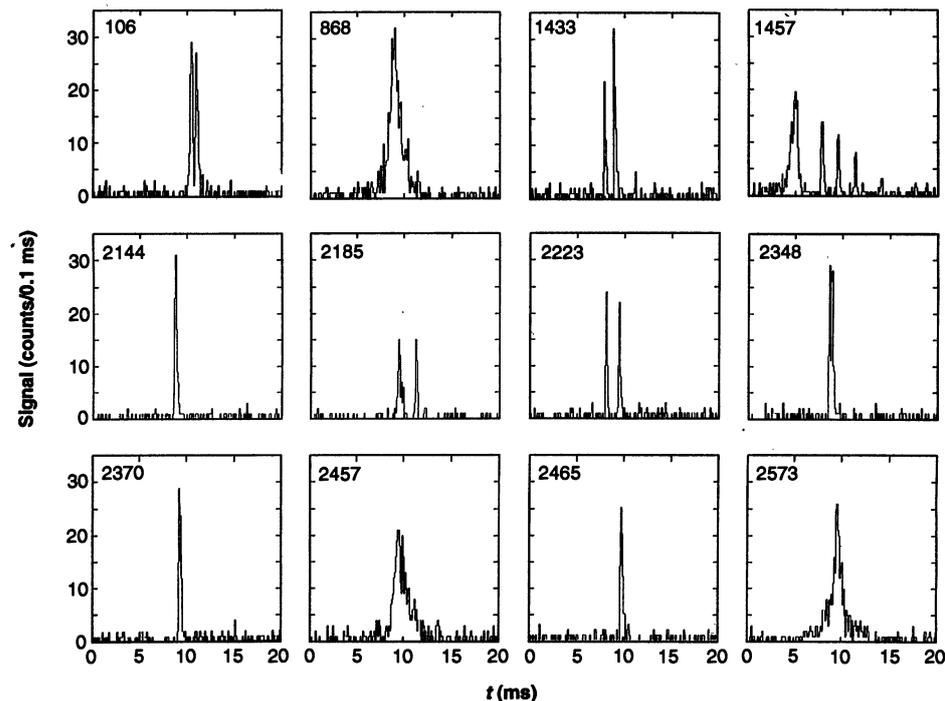


Fig. 4. Time profiles of the events listed in Table 1 (arbitrary start time). The time resolution of the plots is 0.1 ms per bin. Multiple peaks are evident in many of the events, with peak separations from 1 to 4 ms. Typical rise and fall times are ~ 0.1 to 2.0 ms.