

85°C. We employed a Lane-Wells three-prism Raman spectrograph with a reciprocal dispersion of 63A/mm in the region of the exciting line.

Most unexpectedly we obtained by an exposure of 15 hours not only the fundamental Raman frequency, but also the shifts corresponding to the first and second overtones with comparable intensity. The reproduction shown in Fig. 1 is an enlargement of the original spectrum.

The frequencies and relative intensities of the Raman shifts are given in Table I.

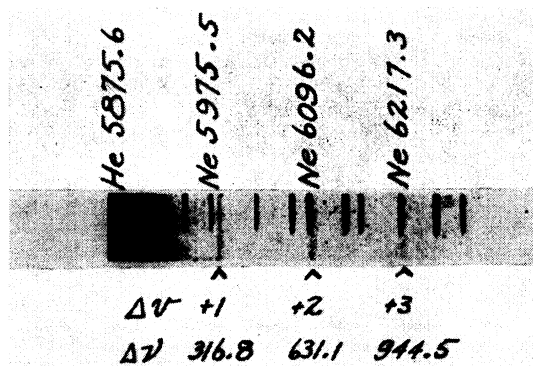


FIG. 1. Raman spectrum of bromine.

From observations on band spectra¹ we have $\omega_e = 323.86 \text{ cm}^{-1}$ and $\omega_e x_e = 1.15 \text{ cm}^{-1}$. From these data we should expect in first approximation a fundamental Raman frequency of 320.4 cm^{-1} as compared with the observed value of 316.8 cm^{-1} . This difference is 3 or 4 times larger than our measuring error. On the other hand, the small anharmonicity of the three observed frequencies agrees very satisfactorily with the above value of $\omega_e x_e$ and confirms our value.

From 316.8 cm^{-1} we calculate for the molecule $\text{Br}^{79}\text{-Br}^{81}$ the uncorrected force constant

$$f = 2.35 \times 10^6 \text{ dynes/cm.}$$

The appearance of the intense overtones is the more surprising when one considers that of all Raman-investigated diatomic molecules the Br_2 molecule approximates best to the simple model of the harmonic oscillator. It seems that even first overtones have never been observed in the Raman spectra of diatomic molecules; in polyatomic molecules they appear in rare cases very weakly. Their intensities compare with the intensities of the fundamental frequencies roughly as the square of the ratio of nuclear distance to displacement. Applying this general rule we should expect in the case of bromine an intensity ratio of nearly $10^6:10^3:1$ between the fundamental frequency and the first and second overtones.

The relative intensities given above were measured by comparing the density of the lines with intensity marks. They do not

TABLE I. Raman lines of bromine.

$\Delta\nu$	$\Delta\nu(\text{cm}^{-1})$	Rel. int.
+1	316.8	1
+2	631.1	0.85
+3	944.5	0.47

represent the true intensity ratio. Reabsorption of the scattered radiation in the bromine gas weakens the fundamental frequency; on the other hand, the spectral sensitivity of the photographic plate employed is somewhat lower in the region of the second overtone. In any case, the true intensities are not very far from those indicated.

There is no doubt that we have here true overtones corresponding to transitions $v = +2, +3$, and not a case of multiple scattering. This results obviously from the relative intensities and also from the observed anharmonicity.

We hope to investigate with a spectrograph of greater dispersion and resolving power the finer vibrational details of the observed frequencies. Besides the isotope effect, we have to expect a structure coming from the participation of the different initial vibrational states. For our temperature conditions the statistical weights of the fundamental and of the first and second excited vibrational states correspond approximately to the ratio 100:45:13. Unfortunately, the absorption of shorter wave-lengths in the bromine gas prohibits the observation of anti-Stokes shifts.

¹ H. Sponer, *Molekülspektren I* (Tabellen, Berlin, 1935).

Decay Time of Stilbene Scintillations as a Function of Temperature

R. F. POST AND N. S. SHIREN
Stanford University, Stanford University, California
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USING 931-A photo-multipliers and a pulsed-counter technique described in the accompanying letter we have photographed scintillation pulses from trans-stilbene and have used these to obtain decay time data at isolated temperatures down to that of liquid nitrogen. The observed pulse rise times were about 10^{-9} second. Since this time is considerably shorter than the measured decay times, the data were analyzed simply by comparison of the photographed pulses (smoothed by tracing) with plotted exponentials. The trans-stilbene was used in crystalline form, and was of high purity. In an attempt to obtain a rough comparison with the work of Kelley and Goodrich¹ we have also analyzed a few counts from a crystal of anthracene of unknown purity, at the same temperatures at which the stilbene data were taken. Our value for the decay constant of anthracene at liquid nitrogen temperature agrees with theirs and also with the value obtained by Collins.² However, at the higher temperatures our values are noticeably lower than those found by Kelley and Goodrich. The explanation of the discrepancy is not known, but it should be noted that the anthracene pulses consistently showed a very ragged structure at room temperature, making the drawing of the exponentials a matter of individual judgment. The stilbene data, on the other hand, were satisfactorily smooth at all of the temperatures. Our results for stilbene and anthracene are given in Table I, together with their r.m.s. deviations from the mean.

In the experimental set-up, the last 2 dynodes of the photo-multiplier were bypassed with 0.0005 microfarad condensers to prevent dynode voltage variations. Further voltage stabilization during the pulses was achieved by using 100-ohm resistors in the dynode divider network, connected by fairly short leads to the tube socket. Two different tubes were used in obtaining the stilbene data, and no appreciable differences were noted in the data obtained from either at the same temperature. No saturation effects were noted in the performance of the photo-multipliers at even the highest scintillation pulse amplitudes. Because of the rapid rise time of the count pulse, delivered from a low impedance source (a terminated 100-ohm coaxial lead) directly to the plates of the oscilloscope tube, it was necessary to use a 100-ohm damping resistor in series with the connection from the coax center con-

TABLE I. Decay time (to $1/e$) in microseconds.

Temp.	-196°C	-78°	27°
Trans-Stilbene	0.0044 ± 0.0005	0.0049 ± 0.0006	0.006 ± 0.001
Anthracene	0.010 ± 0.002	0.018 ± 0.002	0.023 ± 0.005

ductor to the deflecting plate. This damped the shock-excited oscillations of the series resonant circuit comprised of the inductance of internal leads to the deflection plates plus the deflection plate capacity. The RC time constant of this network was then approximately 6×10^{-10} second.

¹ C. G. Kelley and M. Goodrich, *Phys. Rev.* **77**, 138 (1950).

² G. B. Collins, *Phys. Rev.* **74**, 1543 (1948).

Performance of Pulsed Photo-Multiplier Scintillation Counters*

R. F. POST AND N. S. SHIREN

Stanford University, Stanford University, California

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IN an attempt to develop higher speed counting equipment for use with the Stanford linear accelerators, we have applied pulse methods to the operation of scintillation counters with the following results. We have pulsed several 931-A photo-multipliers to voltages as high as 5 kv, without voltage breakdown. Pulse lengths up to 2.5 microseconds have been used, the upper limit being set by the pulser. Using an Ag_{110} gamma-source, we have observed stilbene scintillation counts with a rise time of about 10^{-9} second, and with a maximum height of about 80 volts. The pulses were delivered from the photo-multiplier into 100-ohm RG7U coaxial cable, terminated at its output end. They were displayed by a 5RP11A high voltage cathode-ray tube with no intermediate amplification. The observed rise-times are probably made appreciably longer by transit time and lead inductance effects within the oscilloscope tube.

Not all of the tubes tried withstood the highest pulse voltages, but those that did gave infrequent and small noise counts. There did not seem to be any consistent correlation between excellence of performance at low d.c. voltages and that under high voltage pulse operation. The single 1P21 tube which was tried, though satisfactory at the usual d.c. voltages, happened to be inferior to any of the several 931A tubes tried, from the standpoint of voltage breakdown and noise. However, this tube may not have been representative. A tendency for noise count rates to increase near the end of the longer pulses was noted for all tubes. This suggests that pulsed operation greatly reduces the incidence of that part of the noise due to accumulative ionization effects in the multiplier. It was also found that the use of an external shield, pulsed to the cathode potential strikingly reduced the noise counts.

From an analysis of photographs of individual counts, and by the use of very short delay line clippers, we have established that the rise time of a typical scintillation pulse is 10^{-9} second or less, and that the total duration of single-electron noise pulses is about 5×10^{-10} second, in rough agreement with the value calculated by Sard.¹ At the high voltages employed, effects due to transit time variations should be reduced by more than a factor of two. In addition to the effects of the oscilloscope characteristics on the measured value of pulse lengths, it is probable that the noise pulses are somewhat lengthened by the effect of lead inductances in the photo-multiplier tube itself, since, from Sard's calculation one would expect to find noise pulse durations of about 2×10^{-10} sec. at these voltages. High voltage operation improves the focusing properties of the photo-multiplier,² and increases the current output at which space charge effects become important. This latter fact is borne out by the experimental results. At 5 kv, no saturation effects have been observed, even for output currents approaching one ampere. From the height of the single-electron noise pulses observed, we estimate that the current gain of an average tube is about 10^9 with no saturation up to the highest scintillation pulses observed.

Our pulsing circuit was designed to deliver square pulses of extremely uniform amplitude. However, at the highest pulse voltages used, pulse regulation is less important, since these voltages per stage are near those corresponding to the maximum

of the secondary emission multiplication curve. Although we have not tried pulsing at extreme repetition rates, the evidence to date suggests that this would be entirely feasible, especially if d.c. clearing fields were applied to the tube during the time between the pulses.

The pulsed scintillation counter could be used in the investigation of extremely short-lived isomeric states. We are preparing to carry out experiments of this kind, as a test of the method, by photographing the parent and delayed events as presented on a fast oscilloscope sweep. Beta- and gamma-events will be distinguished by the use of two counters, each connected to a single deflection plate. By placing selective absorbers in front of one of the counters, the gamma-events can be identified from their sense on the oscilloscope trace.

We have also applied the method to the measurement of phosphor decay times, with the results quoted in the accompanying letter. A paper describing the method in more detail, as applied to fast counting and coincidence work, is in preparation.

* The accelerator program is supported by ONR Contract N6onr-25116.

¹ R. D. Sard, *J. App. Phys.* **17**, 768 (1946).

² G. A. Morton, *RCA Rev.* **10**, 525 (1949).

Terphenyl and Dibenzyl Scintillation Counters

R. HOFSTADTER

Palmer Physical Laboratory, Princeton University, Princeton, New Jersey

AND

S. H. LIEBSON AND J. O. ELLIOT

Naval Research Laboratory, Washington, D. C.

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TERPHENYL (*p*-diphenylbenzene) and dibenzyl¹ (diphenyl-ethane) crystals appear to be two useful additions to the class of aromatic materials used in scintillation counters. Some of the properties of these materials have been determined and are given in Table I, where anthracene and stilbene are listed for

TABLE I. Properties of scintillation counters.

	Decay constant	Relative efficiency	Spec-trum	Melting point °C
	(±10 percent)			
Anthracene	3.4×10^{-8} sec.	1.00	4450A	217
Stilbene	1.2×10^{-8} sec.	0.60 ± 0.10	4080 4200	124
Terphenyl—Sample A	1.0×10^{-8} sec.	0.65 ± 0.10	3900	213
Sample B	1.2×10^{-8} sec.		4050 4300	
Dibenzyl—Sample A	1.5×10^{-8} sec.	0.60 ± 0.10	3520	52.5
Sample B	1.7×10^{-8} sec.		3710 3950 weak	

comparison. Each of the new materials forms excellent crystals from the melt. Dibenzyl crystals are remarkably clear although they sometimes crack when taken from the mold. On the other hand terphenyl crystals are rugged and appear to be among the most durable of presently known organic scintillators. We have not yet succeeded in growing colorless terphenyl crystals, the present ones being slightly yellow but clear. It is probable that removal of the impurity producing the yellow coloration will increase the pulse height. The speed, good handling characteristics, and pulse height of terphenyl recommends its use in certain applications of scintillation counters. Dibenzyl has been obtained from the Matheson Company and (yellow) terphenyl from the Eastman Kodak Company.

This work was partially supported by the U. S. Army Signal Corps and ONR.

¹ Previously investigated by W. S. Koski and C. C. Thomas (*Phys. Rev.* **76**, 308 (1949)), who found that this material gave pulses only slightly over background and much poorer than stilbene.