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Autor: Wyard, S.J. / Smith, R.C.
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E.S.R. of Irradiated Frozen H_2O_2 — H_2O Solutions

by S. J. WYARD and R. C. SMITH

Physics Department, Guy's Hospital Medical School, London

INTRODUCTION.

We describe below a series of experiments (not yet completed) in which radicals have been produced in frozen solutions of H_2O_2 in H_2O by a variety of methods. These have yielded a whole series of E.S.R. spectra. We present a qualitative interpretation of this series of spectra which derives it from a single radical; but at this stage of the work we do not attempt to identify the radical.

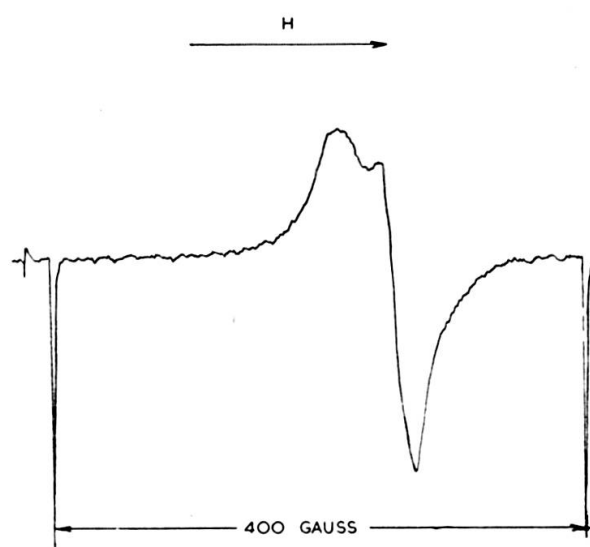
U.V. IRRADIATION.

Solutions of concentrations from 46 to 87% w/w H_2O_2 were used for these experiments, since on rapid freezing they form clear transparent glasses with few or no cracks, and this facilitates quantitative measurements with U.V. irradiation. No attempt was made to de-gas the solutions. The samples were irradiated in quartz tubes at 90° K (temperature of liquid oxygen) and measured in the E.S.R. spectroscope at the same temperature. Using a high pressure mercury arc lamp, filtered by Pyrex glass so that only wavelengths longer than approximately 3,100 Å were transmitted, the spectrum of figure 1 was obtained. This is a first derivative plot, taken on a conventional X-band spectroscope with 280 c/s field modulation.

The samples were then warmed up in stages, by transferring them to a copper block maintained at a given temperature, storing them there for five minutes, and then returning them to the spectroscope for measurement at 90° K. Over a range of warm-up temperature from 120° K to 145° K there was a progressive change in the spectrum, as shown in figure 2, accompanied by a decrease in the total number of spins. The changes in the spectrum consist of a decrease in overall line width, from 80 to 60 gauss, a change in the ratio of the heights of the two low-field peaks, and the appearance of a hyperfine splitting of 11 gauss in the high-field peak. The

ratio of heights of the low-field peaks has been the most useful parameter for comparing spectra, as this varies much more than does the overall line width.

The spectrum obtained before warm-up varies with the U.V. wavelength used, as shown in figure 3. Use of a shorter average wavelength changes the shape slightly, in the same direction as warming up.

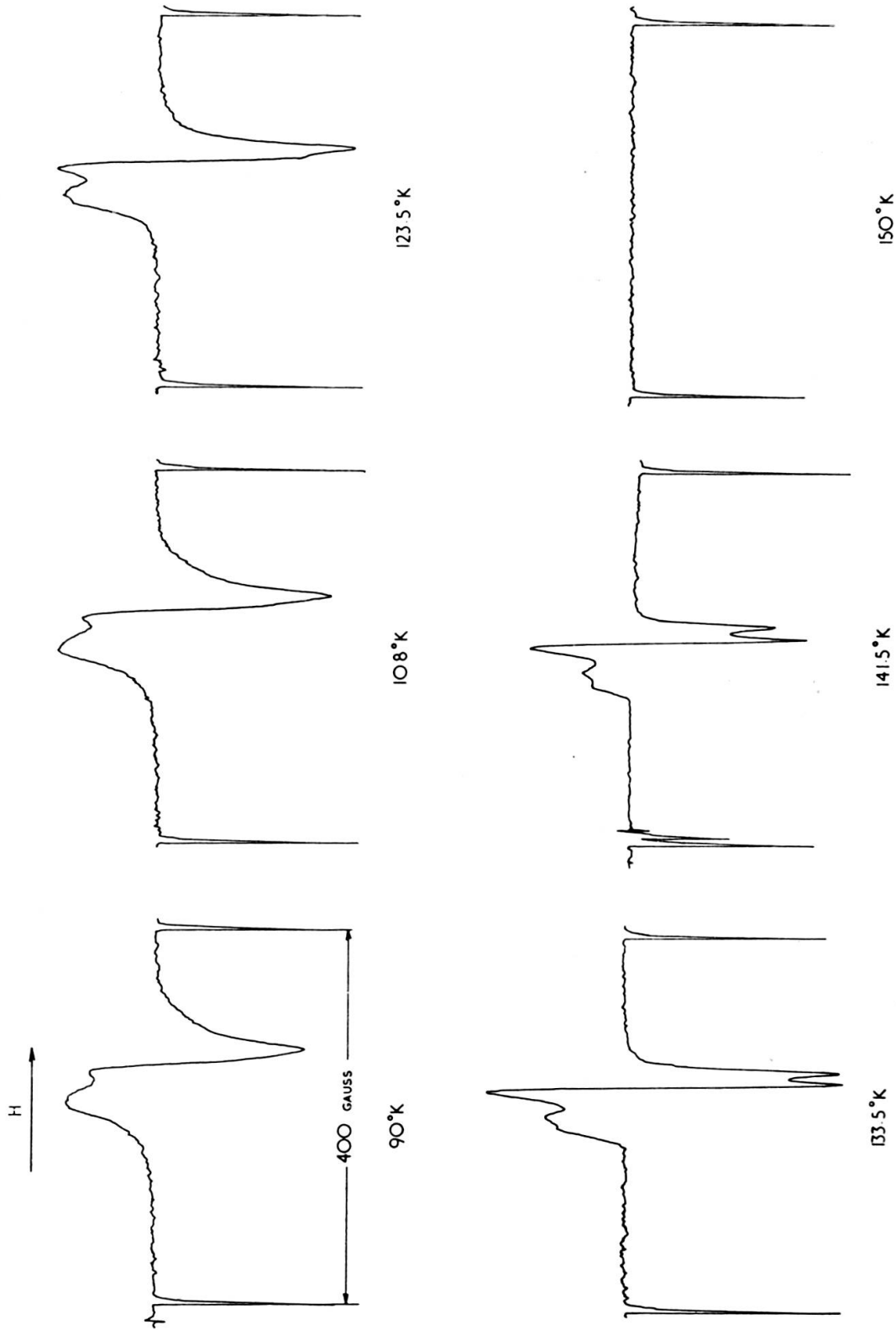


UV IRRADIATION OF H_2O_2 — FIRST DIFFERENTIAL
OF ESR ABSORPTION FROM 87% w/w H_2O_2 AT 90°K
UV WAVELENGTHS $> 3100 \text{ \AA}$

Fig. 1.

IONIZING RADIATIONS.

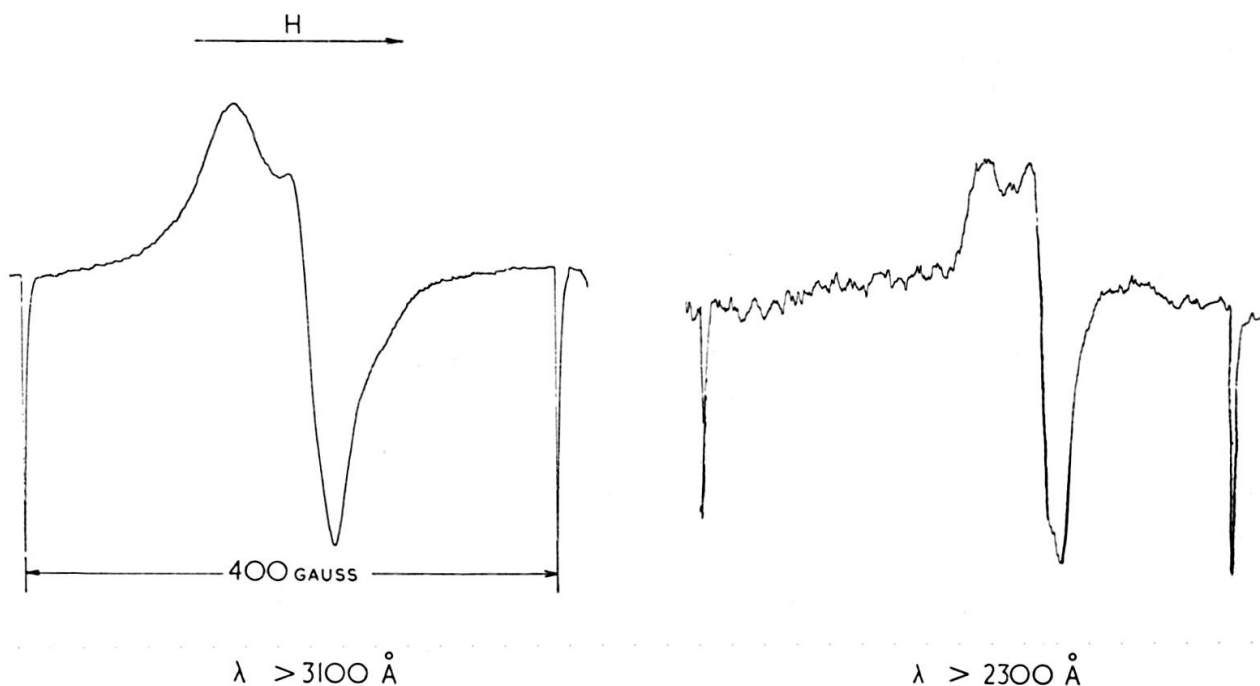
X-rays, electrons from a linear accelerator and deuterons from a cyclotron have been used, and for moderately low concentrations of radicals these all gave the same spectrum, which was intermediate between the extremes of figure 2. With deuterons it was possible to give a very large radiation dose and build up the concentration of radicals to 0.66% of the total number of H_2O_2 molecules present in the sample (i.e., a radical concentration of 10^{-1} M). As the concentration increased above 0.015% the spectrum broadened, as shown in figure 4.



UV. IRRADIATION OF H_2O_2 - WARMING OF H_2O_2 SAMPLE IRRADIATED AT 90°K. SAMPLE STORED AT TEMPERATURE MARKED FOR 5 MINUTES BEFORE RETURNING TO 90°K FOR E.S.R. MEASUREMENT. UV. WAVELENGTHS $> 3100 \text{ \AA}$

OTHER AGENTS

E.S.R. spectra of the same type have been found in the discharge products, collected at 90°K , of radio frequency discharges in both water vapour and in hydrogen peroxide vapour. The spectra obtained were intermediate between the extremes of figure 2, and varied a little with experimental conditions.



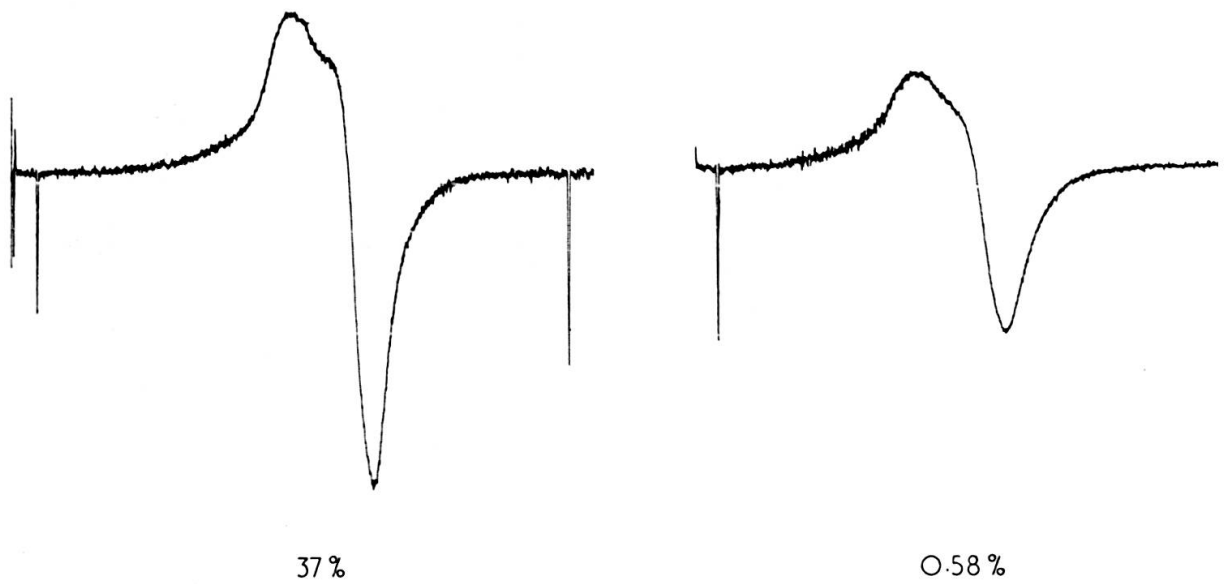
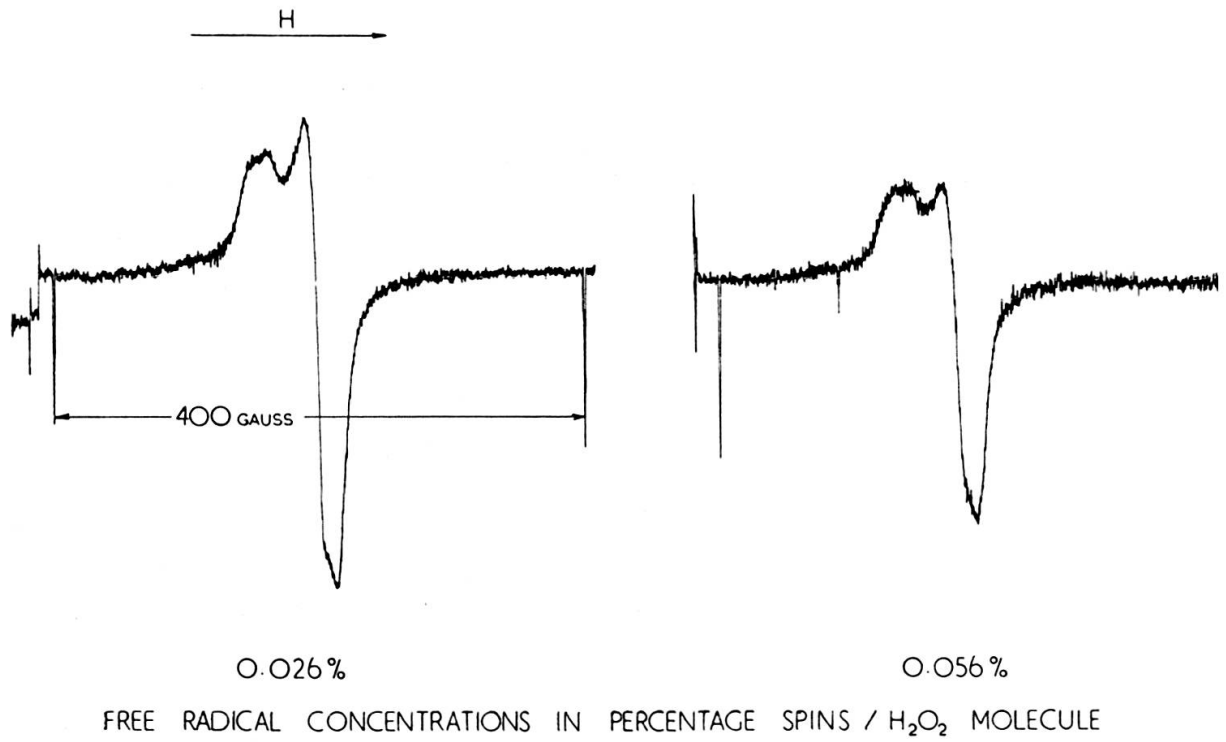
UV IRRADIATION OF H_2O_2 — EFFECT OF DIFFERENT U.V. WAVELENGTHS λ ON SPECTRUM SHAPE FROM 61-62 % H_2O_2 IRRADIATED AT 90°K

Fig. 3.

Hydrogen peroxide-water glasses at 90°K sparked with a Tesla coil also gave similar spectra, again with some experimental variation in shape.

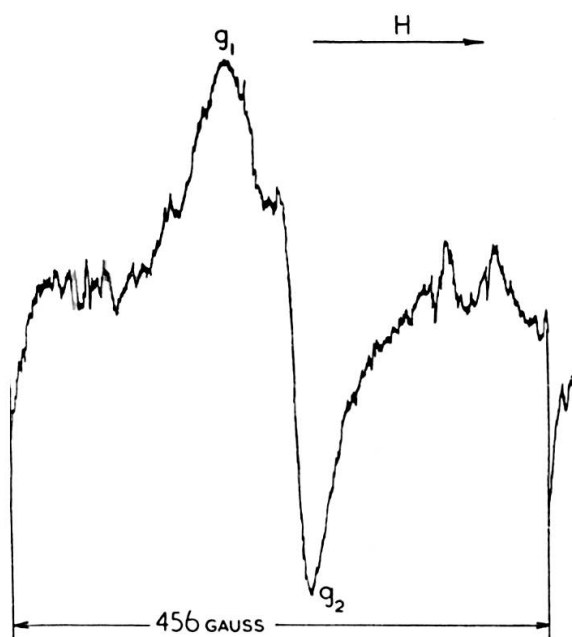
DEUTERIUM EXPERIMENTS.

Some of the above experiments have been repeated using D_2O_2 in D_2O (99% deuterium). The spectra are generally similar to those already shown except that the high-field peak does not show hyperfine splitting on warming



15 MeV DEUTERON IRRADIATION OF H₂O₂—VARIATION OF SPECTRUM SHAPE WITH RADICAL CONCENTRATION FOR 60% H₂O₂. IRRADIATION AT 90°K.

Fig. 4.

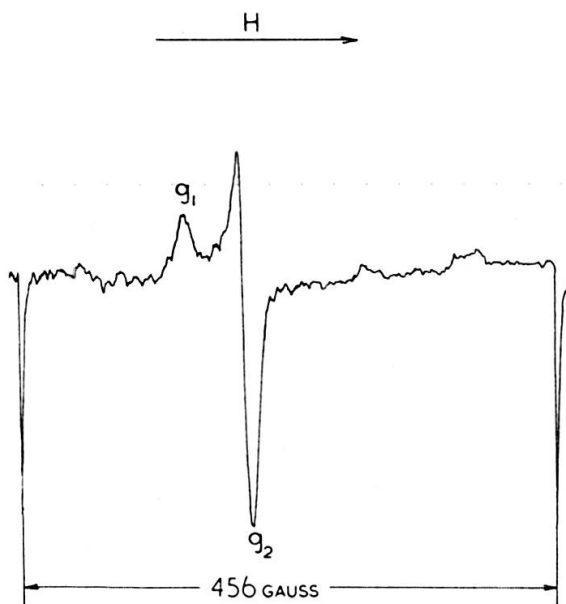


D) 'PRIMARY' SPECTRUM

$$g_1 = g_{11} = 2.04 \pm 0.01$$

$$g_2 = g_1 = 2.00 \pm 0.01$$

$$\text{LINE WIDTH} = 88 \pm 6 \text{ GAUSS}$$



2) 'SECONDARY' SPECTRUM

$$g_1 = g_{11} = 2.0389 \pm 0.0010$$

$$g_2 = g_1 = 2.0044 \pm 0.0004$$

$$\text{LINE WIDTH} = 33.5 \pm 2.0 \text{ GAUSS}$$

$$\text{HYPERFINE SPLITTING} = \text{INSUFFICIENTLY RESOLVED}$$

V. IRRADIATION OF D_2O_2 - DATA FOR E.S.R. FIRST DIFFERENTIALS FROM 80% D_2O_2 OF 90°K IRRADIATION 'PRIMARY' SPECTRUM 2) WARMING AT 133.5°K FOR 5 MINUTES 'SECONDARY' SPECTRUM.

Fig. 5.

up. Figures 5 ($D_2 O_2$ in $D_2 O$) and 6 ($H_2 O_2$ in $H_2 O$) compare the spectra obtained after irradiation by long wavelength U.V., both before and after warming up.

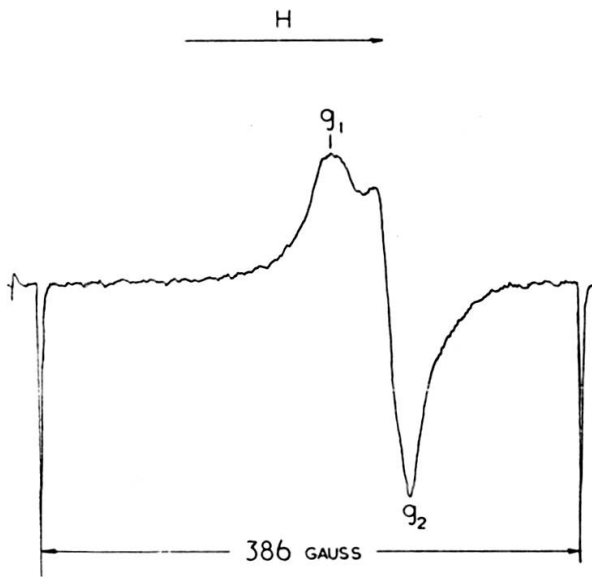
SUMMARY OF SPECTRA OBTAINED.

This is shown in figure 7, where all the experimental spectra are classified according to the peak height ratio. Any of the samples, if warmed up, would eventually produce the narrowest spectrum shown in figure 2.

INTERPRETATION.

The general shape of all the spectra obtained is characteristic of radicals whose g -value is anisotropic but has an axis of symmetry. The low-field peak gives approximately the g -value when the axis is parallel to the applied magnetic field, and the high-field peak gives the perpendicular value. In the case of a deuterated sample after warm-up we have obtained a reasonable fit between the observed spectrum and a calculated one (Fig 8). The calculation assumes a Gaussian line shape with a width of 11 gauss for the single radical, and having $g_{\parallel} = 2.039$, $g_{\perp} = 2.006$. We expect that a similar agreement would be obtained in the case of warmed up samples containing hydrogen, but the calculation is more difficult because of the hyperfine splitting. The spectra from warmed up samples may thus be assigned to a single radical. All the other spectra which have been obtained are believed to derive from this spectrum by means of spin-spin broadening, which widens the line for a single radical without altering the g -values; and this broadening may arise in a variety of ways.

In the case of U.V. irradiation, the primary act consists in the formation of pairs of OH radicals from a single molecule, so that the final radicals, whether OH or some other radicals derived from them, are also likely to occur in pairs. This would account for the broadening, independent of dose, which is observed in the U.V. irradiated samples. If long wavelength U.V. is used, the quantum energy is little more than the dissociation energy for $H_2 O_2$ (2.3 eV. corresponding to 5,400 Å), so there will be little surplus energy available for softening the glass locally and permitting the radicals to diffuse apart. As the quantum energy increases, there is a greater local rise in temperature, and a greater diffusion apart of the two radicals of each pair. Thus the broadest spectrum is obtained with the longest wavelengths, as observed experimentally.

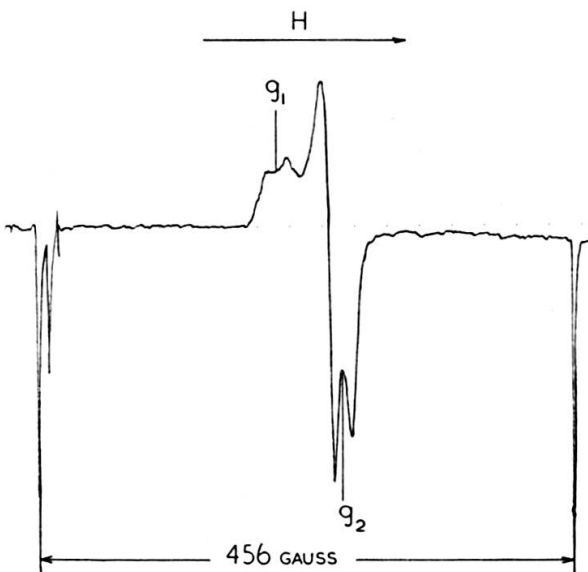


1) 'PRIMARY' SPECTRUM

$$g_1 = g_{11} = 2.0419 \pm 0.0040$$

$$g_2 = g_1 = 2.0002 \pm 0.0007$$

$$\text{LINE WIDTH} = 79 \pm 8 \text{ GAUSS}$$



2) 'SECONDARY' SPECTRUM

$$g_1 = g_{11} = 2.0347 \pm 0.0023$$

$$g_2 = g_1 = 2.0001 \pm 0.0006$$

$$\text{LINE WIDTH} = 60.5 \pm 3.0 \text{ GAUSS}$$

$$\text{HYPERFINE SPLITTING} = 13.5 \pm 3.0 \text{ GAUSS}$$

U.V. IRRADIATION OF H_2O_2 — DATA FOR E.S.R. FIRST DIFFERENTIALS FROM 87% H_2O_2 OF
 1) 90°K IRRADIATION 'PRIMARY' SPECTRUM 2) WARMING AT 1415°K FOR 5 MINUTES
 'SECONDARY' SPECTRUM.

Fig. 6.

Irradiation by X-rays and by electrons produces little clusters of a few ion pairs together, and presumably radicals with a similar distribution. This would account for the initial broadening observed for low and moderate doses. With deuteron irradiation one might expect a further broadening at low doses, due to the close spacing of ions along the tracks, but this has not been observed. The broadening obtained with very large doses of radiation is a straightforward concentration effect.

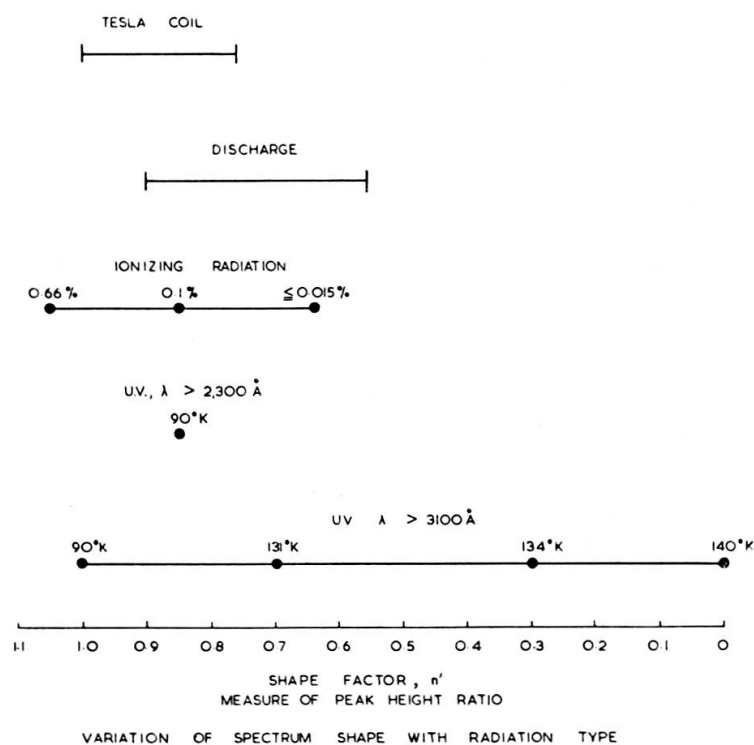


Fig. 7.

Warming up, on this interpretation, is regarded as a process which permits the radicals to diffuse. In the initial stages of warm-up some radicals in the pairs, or clusters, move together and neutralise each other, thus reducing the total number of spins. In the later stages of warm-up one is left with isolated radicals randomly distributed.

We have not yet made numerical calculations of the spectral shapes to be expected from this model for all the different conditions, but the observed broadening, up to about 20 gauss, is certainly of the same order as that produced by radicals spaced a few molecules apart.

If this interpretation of the broadened spectra is correct, all our experiments yield only one radical. This radical has an axially symmetric g -value and contains a proton (or deuteron) to which the unpaired electron is coupled. The radical could well be OH, or HO₂, but there does not seem yet to be sufficient evidence to favour one or the other.

ACKNOWLEDGEMENTS.

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