Comment on ``Paramagnetic Resonance of Alkyl Nitroxides''

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photomultiplier. The signal from the photomultiplier was amplified 1000 times and fed into a Varian 1024 time-averaging computer (CAT). The sweep of the CAT was triggered from the rotating phosphoroscope at the cessation of the excitation period and the photomultiplier output fed into one half of the computer channels. Four-thousand sweeps were taken with the monochromator wavelength set at 7000 Å. A similar series of sweeps was taken with the monochromator set at a second wavelength, the output being fed into the second half of the channels. The complete data were recorded, and the emission intensity at all wavelengths was determined, relative to that at 7000 Å, by comparing the intensity of the emission decay at equal times after excitation shut off. In addition, the triplet lifetime was determined from this time decay. It was found to be equal to that obtained from delayed fluorescence measurements if a monomolecular decay was assumed. It has been shown earlier that at room temperature triplet trapping is negligible,[6] and from this lifetime relation, this emission originates from the free triplet excitons and not from either trapped triplets or impurities. The phosphorescence spectrum corrected for photomultiplier response and stray light is shown in Fig. 1. The latter correction was made by replacing the exit filters by a series having a cutoff at 6000 Å, increasing the photomultiplier time constant to 2 sec, and by recording the output via a dc microvoltmeter. A continuous drive was attached to the wavelength drum of the monochromator, thus giving the complete wavelength range required. The first two peaks were observed together with the tail of the delayed fluorescence. The ratio of peak heights to tail intensity determined the background correction function.

Two progressions corresponding to vibrational frequencies of 1450 cm^{-1} (the peaks at 14 700 cm^{-1}, 13 240 cm^{-1}, and 11 830 cm^{-1}) and 400 cm^{-1} (14 290 cm^{-1} and 12 850 cm^{-1}) are obtained in agreement with phosphorescence spectra for solutions.[4,5]

The spectral origin is shifted to the red by 200 cm^{-1} in the crystal in agreement with the indirectly observed absorption spectrum reported by Avakian *et al.*[6] Since our spectrum was measured at room temperature, this demonstrates again that traps played no part in the observation. The intensity distribution over the vibrational maxima is different from that obtained in absorption.[7] It is not clear whether this is an intrinsic property of the crystal or due to experimental techniques.

The triplet lifetime in the crystal was found to be 22 msec, i.e., practically identical with the triplet lifetime in solid solutions at the same temperature. However, only the purest crystals have such a long triplet lifetime. The relationship between triplet lifetime and phosphorescence intensity has been shown in reference,[3] indicating that the observation of phosphorescence in aromatic hydrocarbon crystals is usually prevented by impurity quenching.

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Comments

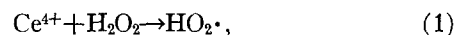## Comment on "Paramagnetic Resonance of Alkyl Nitroxides"
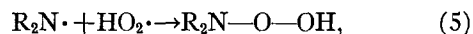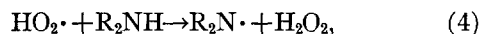
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Recently dialkyl nitroxides have been produced by two methods and their ESR spectra in methanol and chloroform solution described.[1] Similar spectra, apparently of much higher intensity and signal-to-noise ratio, can be obtained in aqueous solution. The presumed sequence of reactions is,[2,3]

$$Ce^{4+} + H_2O_2 \rightarrow HO_2\cdot, \tag{1}$$

$$HO_2\cdot + R_2NH \rightarrow R_2NO\cdot + H_2O, \tag{2}$$

or, less likely, (1) followed by,

$$HO_2\cdot + R_2NH \rightarrow R_2N\cdot + H_2O_2, \tag{4}$$

$$R_2N\cdot + HO_2\cdot \rightarrow R_2N{-}O{-}OH, \tag{5}$$

$$R_2N{-}O{-}OH \rightarrow R_2NO\cdot + \cdot OH. \tag{6}$$

A solution was prepared 1 M in amine, 0.075 M in hydrogen peroxide, and of pH about 8 by dissolving two-thirds of the amine in water, neutralizing to pH 7 with solid carbon dioxide, and adding the remaining amine and hydrogen peroxide. When this solution and 0.05 M ceric ammonium sulfate were drawn through a mixer and ESR flat cell[4] at 5 cm^3 sec^{-1}, excellent simple spectra of high intensity were obtained; for example, in $(CH_3)_2NO$, the extreme outer lines of unit intensity had a signal-to-noise ratio of about 5. The effluent is

a clear, dark brown color, possibly due to the nitroxide. A precipitate is seen if the flow rate is too low.

With dimethyl and diethyl nitroxides the spectral parameters measured in the aqueous solution described at 25°C, and the estimated uncertainties, are

	$a^N (G)$	$a_\beta^H (G)$	g
$(CH_3)_2NO$	17.1±0.3	14.6±0.2	2.0055±0.0001
$(C_2H_5)_2NO$	16.8±0.2	11.6±0.1	2.0054±0.0001

The hyperfine splittings are 10%–20% larger than the corresponding values in chloroform.[1]

When hydrogen peroxide was omitted, no spectra appeared; this differentiates the present reaction from the ceric oxidations of hydrazine[5] and of alkyl hydroxyl-amines.[1]

It is known that the action of OH upon the lower amines in acid solution produces no ESR spectra.[6] Spectra obtained in amine–titanium trichloride–hydrogen peroxide systems of controlled alkalinity are much more complex than those reported here.[7] The nitroxide is almost certainly one component, however.

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Excitation of the He$_{II}$ λ4686-Å Line by Electron Impact*

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The absolute cross section for the production of the He$_{II}$ λ4686-Å ($n=4\rightarrow3$) emission by electron impact on He has been measured in two recent investigations.[1,2] On comparing the two results, there appeared to be slight difference in the shape of the excitation function and a serious difference in the magnitude of the absolute cross sections. (Hughes and Weaver[1] measured 8.2×10^{-21} cm^2 while St. John and Lin[2] measured 4.2×10^{-21} cm^2 for the maximum-line cross section.)

The investigation by Hughes and Weaver was made by simultaneously measuring the excitation function of the He$_{II}$ line and the adjacent He$_I$ λ4713-Å ($4^3S\rightarrow 2^3P$) line. The relative excitation function of the He$_{II}$ line was then placed on an absolute basis by normalizing
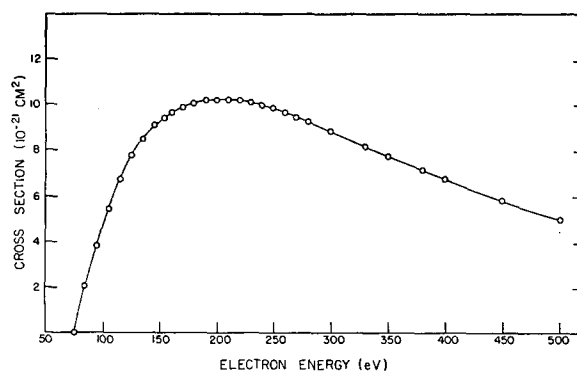

FIG. 1. Excitation cross sections for the He$_{II}$ λ4686-Å line as a function of electron energy. Data taken at a pressure of 10 μ.

the peak of the λ4713-Å excitation to the peak cross section reported by Stewart and Gabuthuler.[3]

We have since remeasured the excitation functions of the two lines with the result that the shape of our λ4686-Å excitation function (Fig. 1) is now in excellent agreement with that of St. John and Lin. Further, the revised cross section of St. John and Lin[4] agrees with our peak value of 10.2×10^{-21} cm^2 to 4%.

In another publication by St. John et al.,[5] absolute
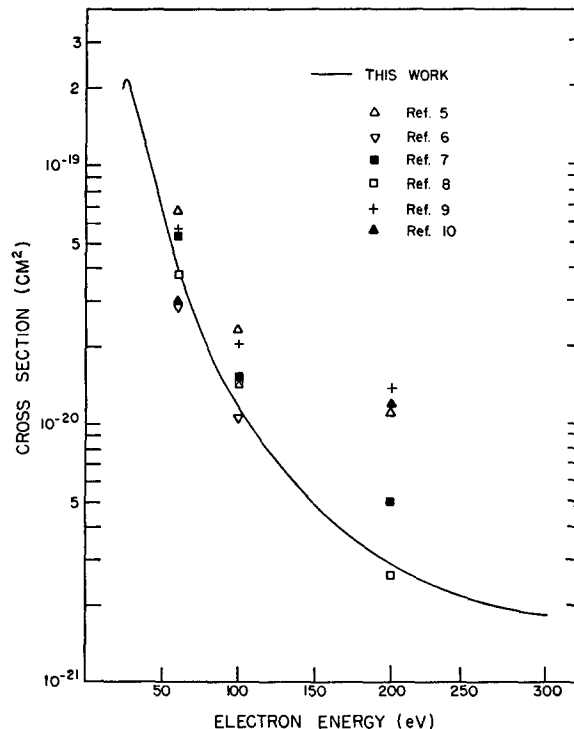

FIG. 2. Excitation cross sections for the He$_I$ λ4713-Å line as a function of electron energy. (Data taken at a pressure of 10 μ. All cross sections have been normalized to the maximum value of 21.9×10^{-20} cm^2 of Stewart and Gabuthuler.)

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