

coupling between the electron spin of O_2 with its rotational angular momentum.⁵ It was then possible to relate Q to an exchange cross section for N- O_2 collisions. This led to an estimate of 1.5×10^{-16} cm², which is a reasonable value for such a cross section.

The amount of power required to saturate the lines should have been proportional to a quantity of the order $W + (1/t_c)$, where t_c is the average time for an atom to flow through the cavity. In this work t_c was of the order of 1 msec and therefore considerably smaller than $1/W$ observed without added O_2 . For this situation, the amount of power required to saturate the lines should depend primarily on the N_2 flow rate. This was indeed observed to be the case.

We have also observed a similar enhancement of unsaturated H-atom signals by small amounts of O_2 . In this case the signal increases were not as great as for N (1.7-fold for 400 cm sec⁻¹ flow rates and 10 ppm O_2). To obtain any H-atom signal at all, however, it was necessary to add traces⁸ of N_2 to the H_2 upstream from the discharge. The smaller degree of enhancement may have been caused by the relaxing effect of discharge produced species.⁵ No detailed experiments were made on this system.

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ESR of Niobium in $CaWO_4$

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THE purpose of this Communication is to report briefly on the Nb resonance occurring as a charge compensator in $CaWO_4$. The importance of Nb in

lowering the threshold for laser action in $CaWO_4:Nd$ has been stressed by Johnson¹ and also by Nassau and Loiacono.² Also Farrar³ has shown that the introduction of charge compensators of the Group Vb elements such as V and Nb produce two extra optical absorption lines on the long-wavelength side of the $^4F_{3/2} \rightarrow ^4I_{9/2}$ transition for Nd^{3+} . To obtain definitive information about charge compensation, we investigated V in $CaWO_4$, and the present Communication is intended as a continuation of this program.

The Nb resonance has been observed in $CaWO_4:Nb$, containing Nd or U. The sample containing uranium was grown from a melt having about 0.5% UO_3 and 1% Nb_2O_5 . The samples were irradiated for about 1 h in the ^{60}Co gamma source (approximately 10^6 rads), and examined in the ESR spectrometer with as little delay as possible.

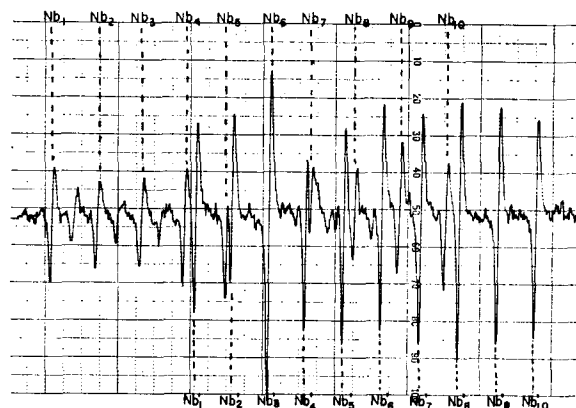


FIG. 1. ESR spectrum of gamma-irradiated $CaWO_4:Nb$ at 77°K. H is along the $[110]$ direction.

A typical spectrum with the magnetic field along the $[110]$ direction taken at 77°K is shown in Fig. 1. In the crystal ab plane, the Nb resonance consists of two groups of 10 lines, corresponding to the nuclear spin $I = \frac{9}{2}$ for ^{93}Nb . For this direction, the g values are 2.009 and 2.039, and the A values are 27 and 29.5 G, respectively, for the two groups. Along the c axis there is a single group of 10 lines with $g = 2.023$ and $A = 29.2$ G. At dry-ice temperature ($-78^\circ C$) the groups coalesce such that $g = 2.026$ and 2.023 along the $[110]$ and $[001]$ directions, respectively. The results are similar to those of V in $CaWO_4$ reported earlier.⁴

The positive Δg and the small hyperfine coupling constant we take as evidence that Nb occupies the covalent W site, as had been inferred from chemical evidence.² Nb resonances have been reported in silicate glasses⁵ ($g_{||} = 1.89$, $g_{\perp} = 1.92$, $A = 310$ G, and $B = 145$ G) and for pentachloromethoxoniobate $[Nb(OCH_3)Cl_5]^{2-}$ in methanol glass and in liquid solutions,⁶ for which the values reported are $g_{||} = 1.965$, $g_{\perp} = 1.809$, $A = 248$ G, $B = 144$ G.

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Postirradiation Scavenging in the Radiolysis of Solid *n*-Hexadecane

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WE have observed postirradiation suppression of the dimer when irradiated solid *n*-hexadecane was dissolved at temperatures below its melting point in 2-methyl-1-pentene, 2-methylpentane, 2-methylpentane with dissolved iodine, ethyl ether, and ethyl ether with dissolved iodine. In each case, *G* (dimer)¹ was reduced to virtually the same level as when dispersed iodine was present during irradiation.

In the radiolysis of solid and liquid *n*-hexadecane, small amounts of added iodine substantially reduced the yield of dotriacontane isomers, and produced appropriate yields of mono-iodohexadecanes.² Accordingly, it was proposed that hexadecyl radicals were the immediate precursors of at least 40% and 70%, the fractions scavenged, of the dotriacontanes in solid and liquid state radiolyses, respectively, and that chemical scavenging by iodine formed iodo-hexadecanes as alternate products. Analogous observations were made for the condensed-phase radiolysis of *n*-heptadecane.³ One drawback to the free radical and chemical scavenging mechanism is that, in the rigid solid, neither large alkyl radicals nor iodine will migrate significantly, and thus will not in general come sufficiently close together to interact to form a dimer or iodoalkanes. To circumvent this objection, it was suggested² that in the solid state proximate alkyl radicals were formed via a hot-hydrogen-atom mechanism in pairs which linked to form the dimer ~60% of the time and that those radicals stable in the solid⁴ near the melting point reacted with each other or with iodine on melting.

As an alternative to melting, dissolution will give to any trapped radicals the mobility required for them to combine or otherwise react. Any changes in product yields from those of the melted irradiated solid should then be due to the solvent, which, if reactive, could

suppress combination [i.e., reduce *G* (dimer)] and yield new and possibly identifiable products.

n-Hexadecane samples were prepared as previously described^{2,5} and irradiated to 4.2 Mrad with 1-MeV van de Graaff electrons on a bed of powdered dry ice at -78°C . Sealed sample tubes were equilibrated at -45° , -36° , -23° , and 0°C in chlorobenzene, ethylene dichloride, carbon tetrachloride, or ice-water melting slushes, respectively. The various solvents listed in Table I were also thermally equilibrated at each temperature prior to being used. The solvents were not degassed and undoubtedly contained significant concentrations of oxygen. The sample tubes were opened after 30 min equilibration and solvent at the appropriate temperature was added in increments with stirring until solution was complete. Each solvent was used at each dissolution temperature. The solutions were left in the thermostating slush for an additional 30 min, warmed to room temperature, and the volatile solvents were evaporated either by standing in a fume hood draft, or more often in a vacuum oven at 45°C . The residual *n*-hexadecane was analyzed gas chromatographically⁵ for the dimer and iodo-hexadecanes when present. For all solvents used, with or without iodine, *G* (dimer) was reduced to virtually the same level as when dispersed iodine was present during irradiation (Table I). *G* (dimer) for the dissolved samples was independent of the temperature of dissolution for all

TABLE I. Dotriacontane and mono-iodohexadecane yields in the radiolysis of *n*-hexadecane at -78°C .^a

Solvent used for dissolution	<i>G</i> (dimer)	<i>G</i> (iodo-hexadecane)
None; melted only	1.4 ^b	...
None; I ₂ dispersed in sample prior to irradiation	0.9	1.4
2-Methyl-1-pentene	1.1	...
Ethyl ether	0.9–1.1 ^c	0.2 ^d
Iodine-saturated ethyl ether	0.9	1.9
2-Methylpentane	0.9	0.1 ^d
Iodine-saturated 2-methylpentane	0.9	1.0
Iodine-saturated ethyl ether ^e	1.2	1.4
Iodine-saturated 2-methylpentane ^e	1.4	0.4

^a Dissolution data are reported for 0.05-ml *n*-hexadecane samples. Similar data for 0.5-ml samples support these results, but are not tabulated because of difficulties arising from the large volumes of solvent required for complete solution at low temperatures.

^b *G* (dimer) at -78°C is 15% lower than that reported² at 4°C , because of the ~130-cal mole⁻¹ activation energy for the over-all processes leading to dimer in the solid radiolysis.^{2,5}

^c *G* (dimer) increased with decreasing temperature between 0° and -45°C .

^d The small amounts of iodo-hexadecanes found in these samples probably arise from contamination of the solvent during evaporation in the vacuum oven. See Footnote 6.

^e These samples were first melted to decay trapped radicals. A large excess of iodine-containing solvent was then added and evaporated as for the dissolved solid samples. See Footnote 6.