The importance of doubly excited configurations is demonstrated by their percent weights in the $^1A_1$ excited states of pyrrole, 1,4-dihydropyridine, and cis-butadiene, these being, respectively, 12%, 37%, and 46%. The corresponding $^1B_1$ excited states have less than 1% doubly excited configurations. We have found that the inclusion of doubly excited configurations is of no particular importance in the lower excited states of styrene, indole, benzofuran, but has moderate effects on 2- and 4-pyridone. Strong effects were observed with various geometrical isomers of aminobutadiene and butadienone. There is still insufficient experimental information to determine if the inclusion of doubly excited configurations is absolutely necessary to rationalize the spectral features of certain types of molecules. Theoretically, it seems hard to justify the arbitrary exclusion of doubly excited configurations. Since both the ground and excited states are affected, the use of the technique requires the adjustment of the parameters in order to produce agreement with experiment. Because of this it is not safe to claim any great theoretical foundation for a particular set of parameters or parameter method.

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Linewidth Variations in ESR Spectra of o-Dinitrobenzene Radicals*

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SEVERAL investigators have discussed linewidth variations in ESR spectra.[1,2] The alternating linewidth effect[3] is particularly interesting. One might suppose that in a radical with several sets of equivalent nuclei, a suitable mechanism could produce broadening similar to the alternating linewidth effect for each set of equivalent nuclei. The possibility then arises of a cancellation of broadening effects for particular lines which could result in ESR spectra with rather unusual linewidth variations. This seems to apply to various o-dinitrobenzene alkali-metal salts.

We assume two states, A and B, presumably due to the position of the cation near one nitro group or the other, for an o-dinitrobenzene alkali-metal ion pair, with rapid exchange between states due to cation motion and equal lifetimes τ. We assume that exchange causes modulation of all three isotropic hyperfine splittings. Thus, for the nitrogens, in A, N_1 has splitting a_1 and N_2 has a_2; while in B, N_1 has splitting a_2 and N_2 has a_1. Similarly, for Protons 3, 6 (Set H_I) and Protons 4, 5 (Set H_{II}). For rapid exchange N_1 and N_2 are equivalent with observed splitting $\bar{a}_N = \frac{1}{2}(a_1 + a_2)$. Similarly, $\bar{a}_{H_I} = \frac{1}{2}(a_3 + a_6)$ and $\bar{a}_{H_{II}} = \frac{1}{2}(a_4 + a_5)$. Cation motion makes Nuclei 1–2, 3–6, and 4–5 instantaneously inequivalent and causes line broadening. The modified Bloch equations[4] or the relaxation-matrix approach[1] can be used to treat the dominant secular effects and a linewidth contribution $T_2^{-1} = \frac{1}{8}\tau[\omega(A) - \omega(B)]^2$ results for the line at mean angular frequency $\bar{\omega}$. These linewidth contributions for the components of each line are given in Table I.

The ESR spectrum of the sodium salt of o-dinitrobenzene in DME at $-40°C$ (see Fig. 1) exhibits only 17 of the possible 45 quartets. We interpret this spectrum as having splitting constants in gauss of $a_{Na} = 0.20$, $a_{H_I} = 0.81$, $a_{H_{II}} = 1.62$, $a_N = 3.90$, and the reduced number of observed lines caused by line broadening effects. The nine quartets with $M_N = 2$ are labelled 1–9 on the spectrum and the broadening of quartets 2, 4, 6, 8 and the resolution of 5 is consistent with the width contributions given in Table I provided $| a_3 - a_6 | \approx | a_4 - a_5 |$. Then lines $(M_{H_I} = \pm 1, M_{H_{II}} = \pm 1)$ are not broadened, lines with either M_{H_I} or $M_{H_{II}}$ zero are broadened, and line $M_{H_I} = M_{H_{II}} = 0$ is composed of two broad components which are not observed and two narrow components due to the cancellation between the terms $(a_3 - a_6)$ and $(a_4 - a_5)$.

For the $M_N = 1$ quartets, labelled 10–18 on the spectrum, the only quartet which seems to be observed is $M_{H_I} = M_{H_{II}} = 0$ which is No. 14. This is consistent with Table I provided we make the additional assumption $| a_1 - a_2 | \approx 2 | a_3 - a_6 |$. All lines with $M_N = 1$ will then

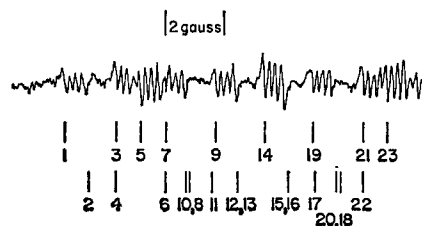
FIG. 1. ESR spectrum of the Na salt of o-dinitrobenzene in DME at $-40°C$. The low-field half of the spectrum is displayed with the beginning of each quartet indexed. The lower set of numbers refer to the positions of the unobserved broadened quartets.

TABLE I. Linewidth contributions.

Proton[a] quantum numbers		Nitrogen $M_N=2$[b]			Quantum $M_N=1$[b]			Numbers[a] $M_N=0$[b,c]		
M_{HI}	M_{HII}	No.[e]	D[f]	Width factor[d]	No.[e]	D[f]	Width factor[d]	No.[e]	D[f]	Width factor[d]
1	1	1			10					$4(a_1-a_2)^2$; (2)
$\bar{1}$	$\bar{1}$	9	1	0	18	2	$(a_1-a_2)^2$	19	3	0; (1)
0	1	2			11					$[2(a_1-a_2)\pm(a_3-a_6)]^2$; (4)
0	$\bar{1}$	8	2	$(a_3-a_6)^2$	17	4	$[(a_1-a_2)\pm(a_3-a_6)]^2$	20	6	$(a_3-a_6)^2$; (2)
$\bar{1}$	1	3			12					$4(a_1-a_2)^2$; (2)
1	$\bar{1}$	7	1	0	16	2	$(a_1-a_2)^2$	21	3	0; (1)
1	0	4			13					$[2(a_1-a_2)\pm(a_4-a_5)]^2$; (4)
$\bar{1}$	0	6	2	$(a_4-a_5)^2$	15	4	$[(a_1-a_2)\pm(a_4-a_5)]^2$	22	6	$(a_4-a_5)^2$; (2)
0	0	5	4	$[(a_3-a_6)\pm(a_4-a_5)]^2$	14	8	$[(a_1-a_2)\pm(a_3-a_6)\pm(a_4-a_5)]^2$	23	12	$[2(a_1-a_2)\pm(a_3-a_6)\pm(a_4-a_5)]^2$; (8) $[(a_3-a_6)\pm(a_4-a_5)]^2$; (4)

[a] Each line in the spectrum is designated by three quantum numbers (M_{HI}, M_{HII}, M_N), no significance is attached to the absolute signs.

[b] In the cases where the width factors have a $\pm$ sign all permutations of sign are allowed and with each permutation there are two components with that width factor.

[c] The numbers in parentheses refer to the number of components which have that width factor.

[d] The linewidth contribution $T_2^{-1}=(1/8)\tau\gamma_e^2$ (width factor).

[e] No. refers to the indexing of quartets on Fig. 1.

[f] D is the total number of components (the degeneracy) of the line.

be broadened except two components of Line 14 where again a cancellation of factors takes place so that the width contribution is zero. Using Table I and the assumed relationships between the differences (a_1-a_2), (a_3-a_6), and (a_4-a_5) we would predict that the pattern of lines with $M_N=0$ should be the same as the pattern with $M_N=2$ and this is what is observed.

Similar linewidth effects occur at low temperatures for the potassium salt.

The relationships between the differences $|a_3-a_6|$, $|a_4-a_5|$, and $|a_1-a_2|$ are introduced here as *ad hoc* assumptions. Calculations indicate however that they are consistent with perturbation of one nitro group by the cation.

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γ Radiolysis of Liquids at High Pressures. II. Aqueous Solutions of Ceric Sulfate

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IN a study of the pressure dependence of yields in γ radiolysis of aqueous ferrous sulfate solutions,[1] the results for deaerated 0.8 N H_2SO_4 solutions suggested, but did not establish, that the primary yields of water radiolysis are invariant as pressure varies from atmospheric to 6.34 kbar. Pressure independence of the primary yields has a very important corollary— namely, an observed pressure dependence of measured yields in radiolysis of aqueous solutions (e.g., aerated ferrous sulfate solutions[1]) is attributable to an effect of pressure on the relative rates of certain secondary reactions. Therefore, to establish conclusively that the primary yields of water radiolysis are independent of pressure, the γ radiolysis of 0.8 N H_2SO_4 solutions of ceric sulfate was studied over the pressure range from atmospheric to 6.4 kbar.

Reagent grade $Ce(HSO_4)_4$ of G. Frederick Smith Chemical Company was used. The purification of water,

cleaning of glassware, analytical techniques for gas products, and the syringe technique for study of the radiolysis of aqueous solutions have been described.[2] The high-pressure system and irradiation techniques were described in the initial paper of this series.[1] Solutions were irradiated at $\sim20°$ in the Notre Dame 10-kCi ^{60}Co facility; the dose rate was $\sim1.6\times10^{16}$ eV $g^{-1}\cdot min^{-1}$ based on $G(Fe^{3+})=15.6$ for the Fricke dosimeter and a molar extinction coefficient at 304 mμ of 2240 $M^{-1}\cdot cm^{-1}$ at 25° (with 0.7% increase per degree).

Aerated solutions of $2\times10^{-4} M$ Ce^{4+} and 0.8 N H_2SO_4 were first irradiated in 100-ml syringes to 50% reduction of Ce^{4+}. It was these solutions which were used for the determination of yields in γ radiolysis as a function of pressure. In the absence of such a preirradiation, a reproducible increase in $G(-Ce^{4+})$ with increase in pressure was observed; study of the dose dependence of ceric reduction, both at atmospheric pressure and 6.4 kbar, revealed that the effect was caused by impurities. Concentrations of Ce^{4+} were determined spectrophotometrically[3] using a molar extinction coefficient at 320 mμ of 5580 $M^{-1}\cdot cm^{-1}$.

Over the applied pressure range from 0 to 6.4 kbar, $G(-Ce^{4+})=2.58\pm0.06$ was obtained for aerated solutions at a dose of 10^{18} eV g^{-1}. Normalization of this value by Boyle's method[4] gives $G(-Ce^{4+})=2.54$, which may be compared with $G(-Ce^{4+})=2.44$ obtained by Boyle as the average of normalized values from a number of different studies at atmospheric pressure. At a dose of 1.5×10^{18} eV g^{-1} to the aerated solutions, $G(H_2)$ was measured to be 0.42 ± 0.01 over the applied pressure range 0–6.4 kbar. For comparison, an atmospheric-pressure value of $G(H_2)=0.43$ is calculated from the Mahlman equation[5] $G(H_2)=0.44-0.21[Ce^{4+}]^{1/3}$ for $[Ce^{4+}]=10^{-4}M$. In deaerated solutions at 1.5×10^{18} eV g^{-1}, $G(O_2)=0.77\pm0.03$ was obtained over the applied pressure range 0–6.4 kbar. This value is about the average of two previous measurements at atmospheric pressure which gave $G(O_2)=0.84$[6] and 0.71.[4]

In γ radiolysis of dilute solutions of ceric sulfate in 0.8 N H_2SO_4, either aerated or deaerated, the measured yields are determined only by the primary yields, denoted by g, as follows:

$$G(-Ce^{4+})=2g(H_2O_2)+g(H)-g(OH), \quad (1)$$

$$G(H_2)=g(H_2), \quad (2)$$

$$G(O_2)=g(H_2O_2). \quad (3)$$

The invariance of $g(H_2)$ and $g(H_2O_2)$ over the pressure range 0–6.4 kbar is established directly by invariance of the measured yields $G(H_2)$ and $G(O_2)$, respectively, cf. Eqs. (2) and (3). The pressure-independent $g(H_2O_2)=0.77\pm0.03$ obtained in this work is in excellent agreement with the pressure-independent $g(H_2O_2)=0.78\pm0.02$ obtained in γ radiolysis of 0.8 N H_2SO_4 solutions of dichromate.[1] To establish the in-