

energy which is a small fixed amount above the ionization threshold. This fixed energy was chosen as 1 eV. The relative ionization probabilities [i.e., relative $i(U+1 \text{ eV})$] that are thus obtained are compared with the experimental data⁶ in Fig. 1. Following Deverse and King, the value for benzene is arbitrarily taken as 200.

In the figure, the open circles refer to substituted benzenes, whose ionization energies were taken from the electron-impact data of Crable and Kearns.⁸ The filled circles give the results for polynuclear aromatics, using the ionization energies calculated by Streitwieser.⁹

Correlation between the experimental and calculated relative ionization probabilities is evident, but several discrepancies also arise. First, the experimental probabilities cover a much broader range than do the calculated values. Second, the results calculated for several families of compounds disagree with experiment. For example, the calculations give relative values for the three xylenes, and for α - and β -methylnaphthalene which are in different orders from the corresponding experimental data.

Although inaccuracies in the experimental data and the ionization thresholds employed undoubtedly contribute to the discrepancies noted, Kington's recent calculations⁵ indicate that the use of better kinetic-energy distributions for the bound electrons is of much greater importance. The fact that the slope of the correlation in Fig. 1 is appreciably different from unity is probably due to the improper threshold behavior predicted by the classical impact approximation.

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ESR Hyperfine Linewidths from Benzene Anion Distortions*

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IT was reported several years ago by Townsend and Weissman¹ that the proton hyperfine structure in the paramagnetic resonance of the anions of benzene, triphenylene, and coronene is unusually broad when compared to the sharp hyperfine structure obtained from most other aromatic hydrocarbons studied under identical conditions. They suggested this broadening may be associated with dynamic Jahn-Teller distortions which would modulate the spin distributions. McConnell and McLachlan² (MM) presented a detailed calculation on the benzene negative ion to demon-

strate that its ground vibronic state is doubly degenerate, and they attributed the anomalously broad benzene anion linewidths to the effects of a fluctuating Stark effect from the polar solvent. They argue that this solvent interaction will remove the ground-state vibronic degeneracy so that the lower energy state is approximated by the molecular orbital

$$\psi = \frac{1}{2}(\phi_1 + \phi_2 - \phi_4 - \phi_6). \quad (1)$$

(Their comments on the spectrum, as well as those presented here are not radically altered by the other choice.) Equation (1) predicts one-quarter of an unpaired electron on each of four carbon atoms and zero on the opposite carbons, 3 and 6. However, the solvent effect, which is random, would shift the distortion so that at different times the nodes are at Carbons 2 and 5 and also at 1 and 4. MM point out that when the switching time τ obeys the condition $\tau \ll 1/2\pi\Delta\nu$, where $\Delta\nu$ is the hyperfine splitting ($|Q|/4 = 15.7 \text{ Mc/sec}$)³ for one of the distorted configurations, that a single spectrum averaged over the three configurations is obtained, and this is consistent with the observed hyperfine splittings of $|Q|/6$ and the intensity distribution of 1:6:15:20:15:6:1. According to MM the broad lines can still arise from the residual effect of the rapid switching, resulting in a line broadening, $\Delta\nu_k \sim (Q/6)^2 2\pi\tau$, so $\tau \sim 10^{-9}$ sec.

The main point of the present publication is to show that such a mechanism *cannot* explain the anomalous broadening of the benzene spectrum. The reason is that this switching mechanism *must* affect the different hyperfine components differently in a manner analogous to the alternating linewidth phenomenon.^{4,5} The observed spectrum, on the other hand, shows no significant linewidth variation among different hyperfine components.¹

The MM model involves random jumps between three dynamically equivalent states, but opposite pairs of protons always have the same splitting, i.e., they are completely equivalent. This model is readily treated within the framework of the linewidth theory given by Freed and Fraenkel.^{6,7} The linewidths resulting from fluctuations of hyperfine splittings are given by Eq. (2.5) of I for the i th component of the k th line:

$$[T_{2i}^{(k)}]^{-1} = \sum_{u,v} j_{u,v}(o) M_u M_v, \quad (2)$$

where u and v denote one of the three completely equivalent pairs of protons, while M_u and M_v are their z components of spin. The spectral densities $j_{u,v}(o)$ are found from Eq. (B5) of I to be:

$$j_{u,u}(o) = -2j_{u,v}(o) = (\tau/18)(\pi Q)^2, \quad v \neq u = 1, 2, 3. \quad (3)$$

The linewidth effects predicted from Eqs. (2) and (3) are summarized in Table I. The last column on the right presents the multiplicative factor of $j_{u,u}(o)$ in the linewidth expression for each of the components

TABLE I. Predicted linewidth contributions from random distortions of the benzene anion.

M^a	M_1, M_2, M_3^b	Degeneracy D_i	$[T_{2,i}^m]^{-1}/j_{u,u}(0)$
± 3	1, 1, 1	1	0
± 2	[1, 1, 0]	6	1
± 1	[1, 0, 0]	12	1
	[1, 1, -1]	3	4
0	0, 0, 0	8	0
	[1, 0, -1]	12	3

$$^a M = \sum_{u=1}^3 M_u.$$

^b Brackets indicate all permutations of the M_u are included.

with degeneracy D_i . Thus, the $M = \pm 3$ lines and part of the $M = 0$ line would be *totally unaffected*. In the limit when such a mechanism is the predominant line-broadening effect, only the $M = \pm 3$, and 0 lines in ratio of 1:8:1 would remain sharp, while the other components would be broadened in differing amounts. It is thus clear that the MM model cannot yield the major contribution to the anomalous broadening in benzene. This conclusion does not necessarily rule out the occurrence of such a mechanism but only requires that $\tau \ll 10^{-9}$ sec. Similar comments apply to coronene and triphenylene.

Line broadening due to modulation of spin-orbit coupling effects^{6,8} would not be in disagreement with the experimental observation that there is no variation amongst the hyperfine lines. Thus, the aforementioned remarks do not affect the spin-orbit mechanism suggested by McConnell.⁸ Work is in progress to test such mechanisms experimentally.

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Absorption, Luminescence, and Excitation Spectra of "Reduced" Fused Silica

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THE presence of a 5.13-eV (242-m μ) absorption band in many "reduced"¹ fused silicas has been known for many years. In addition to this band, a stronger absorption at higher energies which overlaps

the better resolved 5.13-eV band is also seen. The association of these absorptions with the blue luminescence commonly observed in such silicas² has been most recently noted by Hetherington and Jack,³ who utilized the disappearance of both the absorption and luminescence as the glass is oxidized in a study of oxygen diffusion. Furthermore, Cohen⁴ has demonstrated that this band may also be produced by neutron bombardment. The relatively strong, high-energy absorption has not been studied in detail, while the 5.13-eV band has been ascribed to various reduced species.⁵⁻⁷ At the present time, no consensus of opinion seems to exist, and quantitative spectral data correlating one or both of the absorptions with the observed luminescence is meager.

To provide quantitative spectral data, the optical properties of two fused silicas from different sources⁸ were measured, and within experimental accuracy were identical. It is believed that these results would prove typical of such silicas from other sources. Curve 1 of Fig. 1 is the absorption spectrum obtained on the Cary 14 spectrophotometer.⁹ The two absorptions discussed previously are shown here. Curves 2 and 3 are the excitation and emission spectra of the same glass, obtained on the Shoefel spectrofluorometer.¹⁰

The emission spectrum (corrected for photomultiplier response) shows a strong emission at 3.04 eV (408 m μ), of half-width 0.46 eV, as well as a weak 4.28 eV (290 m μ) emission, with the same half-width. Both were pumped at 5.13 eV with monochromatic light and can be pumped with the "short-wave" ultraviolet source found in many laboratories.

The excitation spectra of the two emissions were individually obtained and, when adjusted for the difference in intensity of the two emissions, were identical. The spectrum as plotted is normalized by comparison with sodium salicylate, which has nearly a constant quantum efficiency in the region of interest. It can be seen that the excitation coincides with the discrete absorption band at 5.13 eV. It is not known if the failure of the excitation to return to the baseline at the high-energy side is real, since this is a region of large corrections due to very low intensity of the xenon lamp.

The decay of the 3.04-eV emission intensity with time was obtained. It was exponential and characterized by a time constant equal to 80 μ sec. The correspondence of half-widths in absorption, excitation, and emission as well as the lifetime indicates that the absorption (5.13-eV) and emission (3.04-eV) bands are associated with a single center.

Although previous workers have obtained the necessary reducing conditions in a variety of ways, the effect of extremely small amounts of impurities are uncertain. The results obtained may be explained by several models:

(1) A reduced impurity. Garino-Canina has established a positive correlation between the amount of germanium added to a reduced fused silica and the