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Deuterium Isotope Effects in the Electron Spin Resonance Spectra of Naphthalene Negative Ions*

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(Received 14 April 1967)

High-resolution electron spin resonance spectra have been obtained of the anion radicals of naphthalene and of 10 different deuterium substituted naphthalenes. The ratio of the proton (a^H) to deuteron (a^D) hyperfine splittings was found to be different from the value $a^H/a^D = 6.514$ expected on the basis of the magnetic moments and spins of the two isotopes and, furthermore, it was also found to be different at the α and β positions. These anomalous a^H/a^D ratios have been qualitatively interpreted in terms of vibrational effects which alter the sigma–pi interactions at the substituted positions. The data indicate that the sigma–pi parameters (Q's) for the two isotopes and at the α and β positions are all different, even when account is taken of the magnetic moments and spins. Deuterium substitution at one position was found to alter the hyperfine splittings of the protons at other positions. The magnitude and sign of these changes, which depend on the position and number of substituted deuterium atoms as well as on the position of the proton, have been shown to obey an additivity relationship. The changes in splittings are interpreted as resulting from a redistribution of spin density throughout the radicals. Hückel molecular-orbital calculations have been performed in which the resonance integral for bonds adjacent to a deuterium-substituted position have been altered by a small amount in order to account for this redistribution in spin density. Good agreement between the experimental and calculated changes was obtained, while similar calculations in which the presumed weak electron-donating effect of deuterium was accounted for by a change in the Coulomb integral at the substituted position were in systematic disagreement to a significant extent with the spin densities at certain positions. It was concluded that ESR data provide a more direct means of evaluating the vibrational perturbations introduced by deuterium substitution than do studies of chemical kinetics. Some of the spectra were of such high resolution that anomalies were introduced because of second-order shifts. These could not be analyzed by the usual approximations, and an Appendix is included on the detailed procedures which had to be employed.

I. INTRODUCTION

The simplest model for the alteration of the electron spin resonance spectrum of a free radical by the substitution of a deuterium atom for a hydrogen atom is based on the assumption that all changes result from the different spins and magnetic moments of the two nuclei: The doublet hyperfine splitting caused by the proton ($I = \frac{1}{2}$) is replaced by a triplet from the deuteron ($I = 1$), and the ratio of the proton (a^H) and deuteron (a^D) splittings is given by

$$a^H/a^D = 6.51437, \qquad (1)$$

in correspondence with their respective magnetogyric ratios.[1] Experimental studies of substituted free radicals have shown that this simple model is not completely adequate because additional changes occur in the spectra. Thus, the reduced ratio

$$\kappa = (1/6.514)(a^H/a^D), \qquad (2)$$

is found to deviate significantly from unity,[2–9] with

values between 0.958 and 1.14. The splittings from other nuclei are also affected by the replacement of a hydrogen atom with a deuterium atom; e.g., the ^{13}C or ^{14}N splitting may change by as much as 14% when radicals containing ^{13}C–H or ^{14}N–H bonds are replaced by ^{13}C–D or ^{14}N–D, respectively.[9] In addition, recent observations on the benzene negative ion[10] and the

* This research was supported in part through the U.S. Air Force Office of Scientific Research Grant No. AF-AFOSR-285-65.

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¹ T. F. Wimett, Phys. Rev. **91**, 499 (1953).

² S. Foner, E. L. Cochran, V. A. Bowers, and C. Jen, Phys. Rev. Letters **1**, 91 (1958).

³ T. Cole, J. Chem. Phys. **35**, 1169 (1961).

⁴ R. W. Fessenden and R. H. Schuler, J. Chem. Phys. **39**, 2147 (1963).

⁵ E. L. Cochran, F. J. Adrian, and V. A. Bowers, J. Chem. Phys. **40**, 213 (1964).

⁶ R. W. Fessenden as reported in D. M. Schrader and M. Karplus, J. Chem. Phys. **40**, 1593 (1964); and J. Phys. Chem. **71**, 74 (1967).

⁷ M. R. Das and G. K. Fraenkel, J. Chem. Phys. **42**, 792 (1965).

⁸ J. H. Freed and G. K. Fraenkel, J. Chem. Phys. **38**, 2040 (1963). Other similar radicals have also been studied (W. R. Miller, thesis, Columbia University, New York, 1965).

⁹ The first observation of an anomaly in κ was reported by Cole³ who found $\kappa = 0.986 \pm 0.035$ by studying the NH_3^+ and ND_3^+ radicals at room temperature. He also observed a decrease of 3.7% for the ^{14}N splitting on deuteration. Actually Foner *et al.*,² had observed an isotope effect on the ^{14}N splitting at an earlier date, finding that the nitrogen splitting was 14% greater in the ND_2 radical at 4.2°K than in the NH_2 radical. By comparing the CH_2 radical with the CD_2 radical, Fessenden and Schuler⁴ found $\kappa = 0.9891 \pm 0.0007$, and for the methylene positions of the CH_3CH_2 and CD_3CD_2 radicals they observed $\kappa = 0.990 \pm 0.003$. Fessenden⁶ also discovered that the ^{13}C splitting is reduced from 38.3 G in CH_3 to 36.0 G in CD_3 (a 7% decrease). In the $HC\equiv C$ and $DC\equiv C$ radicals, Cochran *et al.*,⁵ reported $\kappa = 0.958$. Deuterium substitution on nitrogen in the dihydropyrazine and dihydrotetramethyl pyrazine cations⁷ gave $\kappa \cong 0.97$, and a decrease in the ^{14}N splitting on deuterium substitution of from 1.1% to 1.9%. A value of κ greater than unity was found⁴ for the methyl-group splittings in the CH_3CH_2 radical ($\kappa = 1.011 \pm 0.003$), and for the CHD_2CH_2 radical⁴ ($\kappa = 1.178 \pm 0.003$, and the methyl-group proton splittings in the CHD_2CH_2 and CH_3CH_2 radicals are different). A value of κ greater than unity was also obtained for the atoms in an intramolecular hydrogen bond⁸ ($\kappa = 1.14$).

¹⁰ R. G. Lawler, J. R. Bolton, G. K. Fraenkel, and T. H. Brown, J. Am. Chem. Soc. **86**, 520 (1964).

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TABLE I. Analyses of deuterionaphthalene samples and number of hyperfine lines used in determining splitting constants.

Sample[a]	Component	Mole fraction[b]	Number of lines measured[c]
N-1-d	N	0.07	...
	N-1-d	0.93	90 (90)
N-2-d	N	0.50	...
	N-2-d	0.50	76 (90)
N-1,4-d_2	N-1-d	0.10	...
	N-1,4-d_2	0.90	63 (75)
N-2,6-d_2	N-2,6-d_2	>0.97[d]	71 (75)
N-1,4,5,8-d_4	N-α,α-d_2	0.10	6 (75)
	N-1,4,5-d_3	0.19	29 (70)
	N-1,4,5,8-d_4	0.71	28 (45)
N-2,3,6,7-d_4	N-2,3,6,7-d_4	0.51	35 (45)
	N-1,2,3,6,7-d_5	0.29	83 (162)
	N-1,2,3,4,6,7-d_6	0.20	63 (135)
N-d_8	N-d_8	>0.97[d]	63 (81)

[a] Nominal component.

[b] Based on the relative amplitudes of lines in the ESR spectrum assuming equal linewidths for all components. Mole fraction does not include the naphthalene added as an internal standard in all spectra. Estimated errors in mole fractions are 5%–10%.

[c] Only well-resolved lines were used. Figures in parentheses are the predicted number of lines (assuming the assignments of species and splittings to positions as discussed in the text).

[d] Less than 3% of other deuterionaphthalenes would not have been detected.

dihydropyrazine cation[7] have demonstrated that the splittings from *all* of the protons in the radical may be altered by replacing one of them with a deuteron. Collectively, these changes in the spectra which are not produced by the differences in the magnetic properties of the nuclei are referred to as *isotope effects*; it is toward their elucidation that the present work is directed.

The system chosen for study is the naphthalene negative-ion radical and its deuterated analogs. The naphthalene anion permits an evaluation of the isotope effects in aromatic hydrocarbons without complications caused by the presence of orbital degeneracy or heteroatoms, and the large number of possible deuterated naphthalenes provides a stringent test for theoretical interpretations of the effects.

An account of the experimental techniques employed is given in Sec. II, and the results obtained are discussed in Sec. III. An analysis of the variations in proton splittings with deuteration and of the anomalous a^H/a^D ratios is presented in Sec. IV. In Sec. V, theoretical models are considered in which the isotope effects are interpreted as vibrational perturbations of both the pi-electron spin-density distribution and the sigma-pi interactions. An appendix is included on the second-order shifts of line positions observed in some of the naphthalene anion spectra.

II. EXPERIMENTAL PROCEDURES

A. Materials

Naphthalene was taken from stock and purified by sublimination. Naphthalene-1-d, naphthalene-2-d, and naphthalene-1,4-d_2 were prepared from the Grignard reagent of the commercially available bromonaphthalenes. Naphthalene-1,4,5,8-d_4 and naphthalene-2,3,6,7-d_4 were obtained from C. A. Hutchison Jr. of the University of Chicago. Naphthalene-d_8 was obtained from T. H. Brown of the Union Carbide Corporation.

For the preparation of naphthalene-2,6-d_2, it was necessary to synthesize 2,6-dibromonaphthalene. This was accomplished[11] by rearrangement of 1,4-dibromonaphthalene with $AlCl_3$–HCl in CS_2. The product, which was purified by successive recrystallizations from hexane and ethanol, followed by alumina chromatography and then recrystallization again from hexane, had mp 159.0–161.5°C (uncorrected) (the literature mp reported[11] for 2,6-dibromonaphthalene is 159.5–160.5; mp reported for the isomeric 2,3- and 2,7-dibromonaphthalenes are[12] 140.5° and[13] 140°, respectively). The bromo compound was converted to naphthalene-2,6-d_2 by treatment with excess n-butyl lithium in ether followed by quenching with D_2O. The solvent was then removed *in vacuo* and the deuterionaphthalene sublimed out of the residue.

Isotopic analyses of the deuterionaphthalene samples, based on relative line amplitudes in the ESR spectra of the anions, are given in Table I.

1,2-Dimethoxyethane (DME) was used as the solvent. It was purified by successive distillations, first from CaH_2, then from $LiAlH_4$, and finally from the tetracene negative ion.

B. Preparation of the Negative Ions

The technique used was essentially that described by Bolton and Fraenkel[14] for the reduction of aromatic hydrocarbons with alkali metals. It was found that the stability of the radicals was quite sensitive to any impurities introduced either by the metallic sodium or by the naphthalene. The naphthalene was therefore sublimed before use and, as is customary, the sodium was vacuum distilled into the sample tube. Since it was found that some extraneous volatile material was carried over during distillation of the sodium, the sample tube containing the naphthalene was warmed briefly after distillation to release this volatile material. Careful preparation resulted in a solution of the naph-

[11] J. Zalkind and Z. Stetzuro, Ber. **64**, 953 (1931).

[12] H. Franzen and G. Staübel, J. Prackt. Chem. [2] **101**, 58 (1920).

[13] J. Kenner, W. H. Ritchie, and R. L. Wain, J. Chem. Soc. 1937, 1526.

[14] J. R. Bolton and G. K. Fraenkel, J. Chem. Phys. **40**, 3307 (1964).

TABLE II. Hyperfine splittings.[a]

Deuterionaphthalene anion	Proton splittings (G)[b]		Deuteron splittings (G)[b]	
	α Positions	β Positions	α Positions	β Positions
N⁻	$a_1^H = 4.9403 \pm 0.0015^c$	$a_2^H = 1.8253 \pm 0.0011^c$	...	...
N⁻-1-d	$[a_4^H]^d = 4.9247 \pm 0.0020(-15.6)^e$ $[a_5^H]^d = [a_8^H]^d$ $= 4.9558 \pm 0.0015(+15.5)^e$	$a_2^H = 1.8296 \pm 0.0007(+4.3)^e$	$a_1^D = 0.7627 \pm 0.0010$ ...	...
N⁻-2-d	$a_1^H = 4.9428 \pm 0.0022(+2.5)^e$	$[a_3^H]^d = [a_7^H]^d$ $= 1.8457 \pm 0.0023(+20.4)^e$ $[a_6^H]^d = 1.8104 \pm 0.0034(-14.9)^e$	...	$a_2^D = 0.2824 \pm 0.0021$
N⁻-1,4-d_2	$a_5^H = 4.9701 \pm 0.0038(+29.8)^e$	$a_2^H = 1.8304 \pm 0.0019(+5.1)^e$	$a_1^D = 0.7601 \pm 0.0015$	...
N⁻-2,6-d_2	$a_1^H = 4.9441 \pm 0.0015(+3.8)^e$	$a_3^H = 1.8642 \pm 0.0010(+38.9)^e$	...	$a_2^D = 0.2805 \pm 0.0005$
N⁻-1,4,5-d_3	$a_8^H = 4.9538 \pm 0.0035(+13.5)^e$	$a_2^H = 1.8348 \pm 0.0017(+9.5)^e$	$a_1^D = 0.7648 \pm 0.0010$	...
N⁻-1,4,5,8-d_4	...	$a_2^H = 1.8356 \pm 0.0015(+10.3)^e$	$a_1^D = 0.7647 \pm 0.0008$	...
N⁻-2,3,6,7-d_4	$a_1^H = 4.9508 \pm 0.0038(+10.5)^e$	...	...	$a_2^D = 0.2862 \pm 0.0008$
N⁻-1,2,3,6,7-d_5	$[a_4^H]^d = 4.9364 \pm 0.0039(-3.9)^e$ $[a_5^H]^d = [a_8^H]^d$ $= 4.9674 \pm 0.0038(+27.1)^e$	...	$a_1^D = 0.7635 \pm 0.0011$	$a_2^D = 0.2863 \pm 0.0006$
N⁻-1,2,3,4,6,7-d_6	$[a_5^H]^d = 4.9825 \pm 0.0039(+42.2)^e$	...	$a_1^D = 0.7624 \pm 0.0010$	$a_2^D = 0.2879 \pm 0.0008$
N⁻-d_8	...	...	$a_1^D = 0.7658 \pm 0.0005$	$a_2^D = 0.2883 \pm 0.0005$

[a] For convenience the splittings are given as positive numbers; presumably, they are in fact all negative.

[b] Splittings of deuterated radicals are relative to the α splitting of the ordinary naphthalene anion used as an internal standard, and the average error in this splitting is not included in the figures given for these compounds. Errors are twice the standard deviation computed from the regression analysis. The α-proton splittings not listed in the table are identical to the α-proton splitting given; the α-deuteron splittings not listed are also identical to the α-deuteron splitting given. The same applies to the β-proton and deuteron splittings.

[c] Errors for the N⁻ splittings are twice the root-mean-square standard deviation of seven samples divided by $(7)^{1/2}$.

[d] See text, Sec. IV, for discussion of assignments.

[e] Figures in parentheses give change in milligauss relative to the corresponding proton splitting in N⁻.
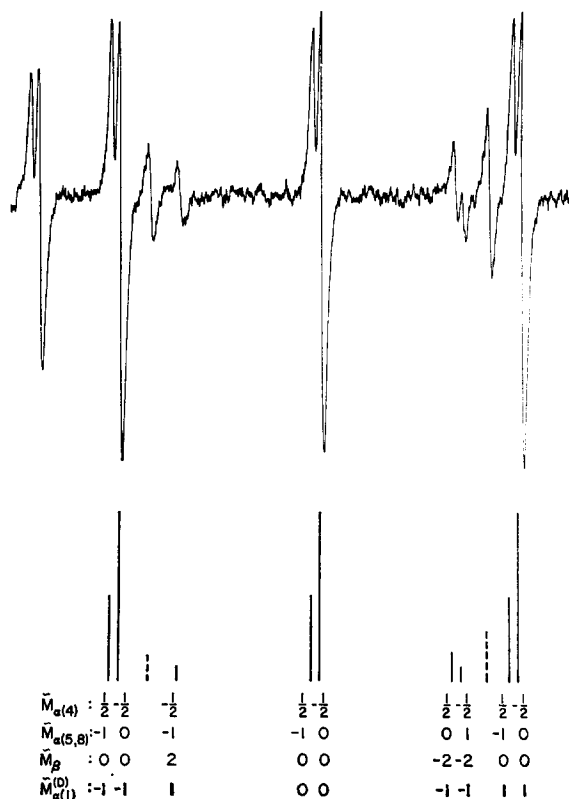
FIG. 1. Portion of the first derivative of the ESR spectrum of the naphthalene-1-d anion radical showing the inequivalence of the proton hyperfine splittings at Positions 4 and 5,8. The spectral-index numbers[23] $\tilde{M}_{\alpha(4)}(\pm\frac{1}{2})$ and $\tilde{M}_{\alpha(5,8)}(\pm1,0)$ are for the proton splittings from the α positions 4 and 5,8, respectively; $\tilde{M}_\beta(\pm2, \pm1, 0)$ is for the proton splittings from the β positions 2,3,6,7; and $\tilde{M}_{\alpha(1)}{}^{(D)}(\pm1, 0)$ is for the deuteron splitting from position 1. If $a_4{}^H$ were the same as $a_5{}^H = a_8{}^H$, the pairs of lines for $\tilde{M}_{\alpha(4)} = \pm\frac{1}{2}$ corresponding to $\tilde{M}_{\alpha(4,8)} = \tilde{M}_{\alpha(4)} + \tilde{M}_{\alpha(5,8)} = \pm\frac{3}{2}, \pm\frac{1}{2}$ would be degenerate. Three sets of split lines are shown for $\tilde{M}_{\alpha(4,5,8)} = -\frac{1}{2}$ and one set for $\tilde{M}_{\alpha(4,5,8)} = \frac{1}{2}$. One (unsplit) line is shown for $\tilde{M}_{\alpha(4,5,8)} = -\frac{3}{2}$. The lines in the reconstruction which are dotted are from the undeuterated naphthalene anion added as a standard. See text for discussion of the assignments. The magnetic field increases to the right.

thalene negative ion[15] N^- in DME which was stable for several weeks.

C. ESR Measurements

An X-band superheterodyne spectrometer was employed[14,16,17] with a Varian Model V-4012-3B 12-in. electromagnet. The magnet was provided with a Varian Model ¦V-3506 magnet-flux stabilizer and wide-range field-scanning equipment. A frequency-stabilized, variable-frequency, proton-resonance oscillator was used to calibrate the field scan for each spectrum. First-derivative spectra were obtained by using 1000-cps field modulation.

[15] We use N^- as an abbreviation for the naphthalene negative ion, and $N^--\alpha, \beta, \cdots, -d_n$, for the deuterionaphthalene negative ions.

[16] J. M. Hirshon and G. K. Fraenkel, Rev. Sci. Instr. 26, 34 (1955).

[17] J. Gendell, J. H. Freed, and G. K. Fraenkel, J. Chem. Phys. 41, 949 (1964).

For some spectra the microwave frequency was monitored throughout the time that a spectrum was run in order to correct for frequency drifts.[18] This was accomplished with a Dymec Model 2650A oscillator synchronizer, and a frequency counter. Some data on the N^- and N^--d_8 radicals[15] were obtained using line-by-line measurements of both the proton and microwave frequencies as described in the Appendix.

The sample temperature was controlled to better than $\pm1°C$. Samples were contained in cylindrical Pyrex tubes of 3 mm i.d. (nominal).

Observation of the small ($\sim10-30$-mG) changes which result on deuterium substitution requires high-quality ESR spectra. Narrow lines (~20 mG) and good signal-to-noise ratios were obtained routinely by optimizing the concentration,[14] temperature, microwave power, and field-modulation amplitude. A temperature of $-60°C$ was employed, and the level of microwave power incident on the cavity was about 1 μW. (The cavity Q, which was not measured, was probably about[19] 1500-2000.)

In order to minimize errors introduced by uncertainties in the field calibration and by microwave frequency drift, splittings of the deuterionaphthalene ions were measured relative to those of undeuterated N^- by adding the latter to the samples as an internal standard in all runs. The procedures for the measurement of line position, the calculation of the "stick plot," and the final least-squares analysis for the splitting constants, have been described previously.[14] The number of lines used in the least-squares analysis for each compound is given in Table I.

III. EXPERIMENTAL RESULTS

A. Hyperfine Splittings and Description of the ESR Spectra

The hyperfine splittings are listed in Table II. Those for N^- are the average of absolute measurements on seven different samples made over a period of nine months. Particular qualitative features of interest in the different spectra are discussed in the following sections.

1. Naphthalene Anion (N^-)

All but one of the many samples of N^- examined at various times had the usual 25-line spectrum arising from the α- and β-proton splittings. Each of these gives sets of lines with intensity ratios $1:4:6:4:1$ corresponding to[20] $M_\alpha, M_\beta = 0, \pm1, \pm2$. The one different sample, which was prepared from material isolated during the

[18] R. G. Lawler, M. R. Das, L. C. Siew, and G. K. Fraenkel (unpublished).

[19] This is the loaded Q with the sample in place, i.e., Q_{LE}. See G. K. Fraenkel in Technique of Organic Chemistry, A. Weissberger, Ed. (Interscience Publishers, Inc., New York, 1960), 3rd ed. (Physical Methods of Organic Chemistry, Vol. 1, Part IV, Chap. 42).

[20] The quantum numbers M_α and M_β are the values of the field-direction components of the nuclear-spin angular momenta of the four α and four β protons, respectively.

course of an attempted replacement of halogen by deuterium in 2,6-dichloronaphthalene, also had the 25-line spectrum, but the lines were so narrow ($\sim$15 mG width between extrema of the first derivative) that the different components shifted by second-order effects[21] were partially resolved. The classification and analysis of this spectrum is discussed in the Appendix. The data for N^- in Table II does not include the measurements on this sample.

2. Naphthalene-1-d Anion $(N^-\text{-}1\text{-}d)$

To a good approximation, the spectrum is that which would be expected if the only effect of deuterium substitution were a change in the spin and magnetic moment of an α proton. Thus, there are four lines with a large splitting and relative intensities 1:3:3:1 (corresponding to $M_\alpha = \pm\frac{3}{2}, \pm\frac{1}{2}$) arising from the three α protons, and these are split into a quintet with relative intensities 1:4:6:4:1 (corresponding to $M_\beta = \pm 2$, ± 1, 0) by the four β protons. Finally, the single deuteron splits the lines into triplets of equal intensity to give a spectrum with a total of 60 lines. Careful examination of each quartet splitting shows, however, that the $M_\alpha = \pm\frac{1}{2}$ lines are split into two lines, as can be seen from the portion of the spectrum presented in Fig. 1. This splitting is present because the three α protons are not exactly equivalent. As shown by the reconstruction in Fig. 1, two of the α protons are equivalent and have a slightly larger splitting than the third. There is no resolvable inequivalence of the four β protons.

3. Naphthalene-2-d Anion $(N^-\text{-}2\text{-}d)$

The same features are exhibited in the ESR spectrum of this radical as were found in the spectrum of the naphthalene-1-d anion except that now the β-proton splittings are inequivalent and there is no resolvable difference in the α-proton splittings. The doublet β-proton splitting is slightly less than the triplet β-proton splitting, as is shown in Fig. 2.

4. Naphthalene-1,4-d_2 Anion $(N^-\text{-}1,4\text{-}d_2)$

With naphthalene as an internal standard, a difference is evident in the position of the lines arising from the α protons in N^- and the two α protons in N^--1,4-d_2; and the α-proton splitting is larger in the deuterated than in the undeuterated radical. Further inspection of the spectrum shows that the β-proton splittings are also larger in the deuterated than in the undeuterated compounds. This effect can be noted by examining the differences between the positions of lines having spectral-index numbers[22,23] $\tilde{M}_\alpha = +1$, $\tilde{M}_D = 0$, in the

[21] R. W. Fessenden, J. Chem. Phys. **37**, 747 (1962).
[22] J. H. Freed and G. K. Fraenkel, J. Chem. Phys. **40**, 1815 (1964).
[23] The spectral-index number $\tilde{M}_i$ is equal to the quantum number M_i except for sign and is defined to be positive on the high-field side of the spectrum, i.e., $\tilde{M}_i = -(a_i/|a_i|)M_i$, where a_i is the associated hyperfine splitting.
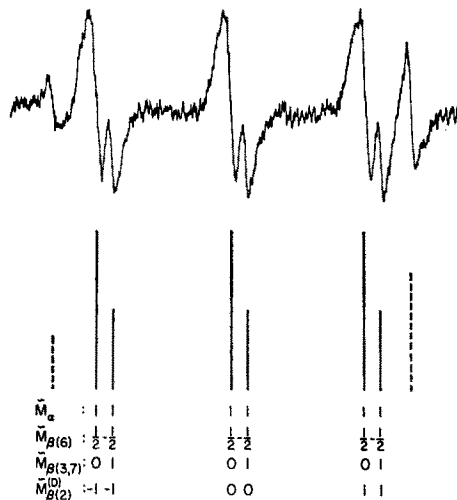

FIG. 2. Portion of the first derivative of the ESR spectrum of the naphthalene-2-d anion radical showing the inequivalence of the proton hyperfine splittings at Positions 6 and 3,7. The spectral-index numbers[23] $\tilde{M}_{\beta(6)}(\pm\frac{1}{2})$ and $\tilde{M}_{\beta(3,7)}(\pm 1, 0)$ are for the proton splittings from the β positions 6 and 3,7, respectively; $\tilde{M}_\alpha(\pm 2, \pm 1, 0)$ is for the proton splittings from the α positions 1,4,5,8; and $\tilde{M}_{\beta(2)}^{(D)}(\pm 1, 0)$ is for the deuteron splitting from position 2. If a_6^H were the same as $a_3^H = a_7^H$, the pairs of lines for $\tilde{M}_{\beta(6)} = \pm\frac{1}{2}$ corresponding to $\tilde{M}_{\beta(6)} = \tilde{M}_{\beta(6)} + \tilde{M}_{\beta(3,7)} = \pm\frac{3}{2}, \pm\frac{1}{2}$ would be degenerate. Three sets of split lines are shown, all for $\tilde{M}_{\beta(3,6,7)} = \frac{1}{2}$. The lines in the reconstruction which are dotted are from the undeuterated naphthalene anion added as a standard. See text for discussion of assignments. The magnetic field increases to the right.

N^--1,4-d_2 spectrum and the lines having the same values of $\tilde{M}_\beta$ with $\tilde{M}_\alpha = +1$ in the N^- spectrum. These differences in line positions, $\Delta(\tilde{M}_\beta)$, are

$$\Delta(\tilde{M}_\beta) = (+1)(|a_\alpha'| - |a_\alpha|) + \tilde{M}_\beta(|a_\beta'| - |a_\beta|),$$

where the primes refer to the deuterated compound. It is found that this small difference increases toward high fields, i.e., as $\tilde{M}_\beta$ becomes more positive. Since $|a_\alpha'| > |a_\alpha|$, this result implies that $|a_\beta'| > |a_\beta|$. There is again no resolvable inequivalence of the four β protons.

5. Naphthalene-2,6-d_2 Anion $(N^-\text{-}2,6\text{-}d_2)$

A situation completely analogous to that for the N^--1,4-d_2 radical holds for this spectrum: The β proton splittings in the deuterated and undeuterated radicals are different and the separations between the lines arising from the α splittings for $\tilde{M}_\beta = +1$ in the two compounds is larger at the high-field end of the spectrum.

6. Naphthalene-1,4,5,8-d_4 Anion $(N^-\text{-}1,4,5,8\text{-}d_4)$

A large number of lines in addition to those expected were found in this spectrum. The principal ones were certainly those of N^--1,4,5,8-d_4, but a careful analysis of the extra lines showed the presence of significant amounts of a radical with three deuterons in α positions as well as another radical with two deuterons in α

positions. The first is thus the $N^- $-1,4,5-$d_3$ anion and the second had splittings (based on measurements of a small number of lines) identical to those of the $N^- $-1,4-$d_2$ anion.[24] This sample consequently provided data for the $N^- $-1,4,5,8-$d_4$, $N^- $-1,4,5-$d_3$, and $N^- $-1,4-$d_2$ radicals. The relative amounts of the three deuterated naphthalenes, assuming equal linewidths, are given in Table I.

7. Naphthalene-2,3,6,7-d_4 Anion ($N^- $-2,3,6,7-$d_4$)

As with the $N^- $-1,4,5,8-$d_4$ sample, many additional lines were detected in this spectrum, and the additional species[24] were identified as $N^- $-1,2,3,6,7-$d_5$ and $N^- $-1,2,3,4,6,7-$d_6$. The assignment of one set of lines to the first of these radicals is unambiguous, but that for the second set depends on the consistent interpretation of the effects of deuterium substitution developed in Sec. IV. The spectrum of $N^- $-1,2,3,6,7-$d_5$ shows the same features as the spectrum of $N^- $-1-$d$, namely a splitting of the $M_\alpha = \pm\frac{1}{2}$ lines of the α-proton quartet. The relative amounts of these three radicals present in the sample are given in Table I.

8. Naphthalene-d_8 Anion ($N^- $-$d_8$)

This sample was essentially pure $N^- $-$d_8$.

B. Second-Order Shifts and g Values

A byproduct of the least-squares procedure of calculating splitting constants is a very precise determination of the position of the center of the spectrum. The calculated centers of all of the spectra of the deuterionaphthalenes recorded were within ± 5 mG of the center of the undeuterated N^-, which implies that the g value is not appreciably altered by deuteration. Precise determination of the g-value difference cannot be accomplished, however, without making corrections for second-order shifts,[21,25,26] and since certain subtleties arise that are not relevant to the main subject under discussion, the details of these corrections are presented in the Appendix. Additional measurements on both N^- and $N^- $-$d_8$ are also described there.

C. Linewidths

Except for two spectra, the linewidths of the deuterated and undeuterated radicals were the same. They all had widths (full width between extrema of the first-derivative spectrum) of about 20 mG. One possible exception was $N^- $-$d_8$, in which several lines appeared to have widths closer to 15 mG than to 20 mG. No attempts at careful width measurements were made, however, and differences of even 10%–20% have not

been considered significant. As indicated above, one sample of the naphthalene negative ion had even narrower lines, perhaps between 10 and 15 mG, and partially resolved components shifted by second-order effects[21,25] were observed.

Width variations within a spectrum were negligible, the standard deviations of the fit of relative line amplitudes to degeneracies being about 5%–10% for both deuterated and undeuterated compounds.

IV. ANALYSIS OF EXPERIMENTAL RESULTS

It is clear from Table II that deuterium substitution causes two effects on the spectrum of the naphthalene negative ion: the proton splittings at the undeuterated positions are altered, and the ratio of the proton to the deuteron splitting is different from the ratio $(a^H/a^D) = 6.514$ expected on the basis of the magnetic moments and spins of the two nuclei. The former changes are of two types, and we designate as *effects of the first type* those produced by α substitution (β substitution) on the proton splittings at other α positions (β positions). *Effects of the second type* are those produced by α substitution (β substitution) on the proton splittings at the β positions (α positions).

A. The Effect of Deuteration on the Splittings at Undeuterated Positions

The data in Table II show that substitution of a single deuterium atom at an α position of N^- causes the splittings of two of the remaining α protons to increase by 15.5 mG while the third splitting decreases by 15.6 mG. Similarly, β substitution causes two of the β-proton splittings to increase by 20.4 mG while the third decreases by 14.9 mG. Additional substitutions cause comparable changes. Since these effects are very small, they might be expected to obey an additivity relationship similar to those observed for methyl-group and chloro substitution in the semiquinones,[27] and for methyl-group substitution in the pyrazine cations.[28] An additivity relationship requires that the substitution of deuterium atoms at positions i and j produces a change in the splitting at position k equal to the algebraic sum of the effects observed at k in radicals which are substituted only at i or only at j. Such a relationship would be important both for the theoretical interpretation of the isotope effect and for the assignments of splittings to positions in cases where unequivocal results cannot be obtained from the spectra alone.

We first consider substitution at α positions. The three possible assignments of the splittings in the $N^- $-1-$d$ radical are shown in the upper half of Fig. 3, and the splittings predicted for the $N^- $-1,4-$d_2$ radical on the assumption of additivity are given in the lower half of

[24] The presence of these impurities is not unreasonable when considered in light of the procedures probably used to synthesize the deuterated compounds.

[25] G. K. Fraenkel, J. Chem. Phys. **42**, 4275 (1965).

[26] B. G. Segal, M. Kaplan, and G. K. Fraenkel, J. Chem. Phys. **43**, 4191 (1965).

[27] B. Venkataraman, B. G. Segal, and G. K. Fraenkel, J. Chem. Phys. **30**, 1006 (1959).

[28] B. L. Barton and G. K. Fraenkel, J. Chem. Phys. **41**, 1455 (1964).

the figure. The experimental result of +29.8 mG is seen to be in excellent agreement with the prediction of +31.0 mG based on Assignment A, while it disagrees with both of the other assignments. Carrying the argument further shows that all three of the N^--1-d assignments predict a splitting of +15.4 mG in N^--1,4,5-d_3, in good agreement with the experimental value of +13.5 mG. A corresponding use of additivity based on Assignment A and the N^--1-d and N^--1,4-d_2 radicals gives 14.2 mG for N^--1,4,5-d_3. Similarly, N^--1,2,3,6,7-d_5 and N^--1,2,3,4,6,7-d_6 can be compared with N^--2,3,6,7-d_4. The latter radical has α-proton splittings that are 10.5 mG larger than in N^-, so that the prediction from Assignment A is that two of the α-proton splittings in N^--1,2,3,6,7-d_5 should be increased by $10.5+15.5=+26.0$ mG while one should be changed by $10.5-15.6=-5.1$ mG, as compared to the experimental results of +27.1 and −3.9 mG, respectively. For N^--1,2,3,4,6,7-d_6, only Assignment A fits, with a value of 41.5 mG; the experimental result is +42.2 mG. This argument has been used, in fact, to identify one of the spectra found in the mixture resulting from the sample of N-2,3,6,7-d_4 as that of the N^--1,2,3,4,6,7-d_6 radical. The other possibilities are N^--1,2,3,5,6,7-d_6 and N^--1,2,3,6,7,8-d_6, and for both of these radicals, Assignment A leads to a predicted shift of +10.4 mG as compared to the experimental value of +42.2 mG.

An additivity relation also holds for the β positions. The three possible assignments of the β-proton splittings in the N^--2-d radical are shown in Fig. 4, together with the predicted values of either +40.8 or +5.5 mG for N^--2,6-d_2. Assignment D is consequently in good agreement with the experimental value of +38.9 mG.

The additivity relationship thus gives an excellent account of the variations of the splittings within a given set, i.e., of effects of the first type. Since only Assignments A in Fig. 3 and D in Fig. 4 are in accord with the data for the α- and β-proton splittings, respectively, they have been taken to be correct and
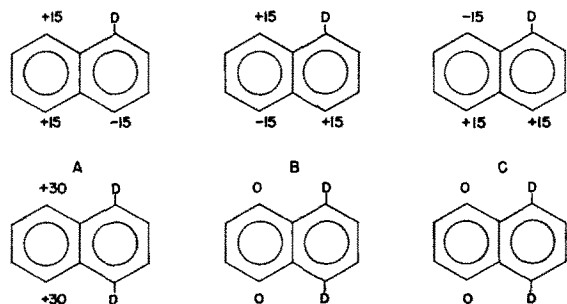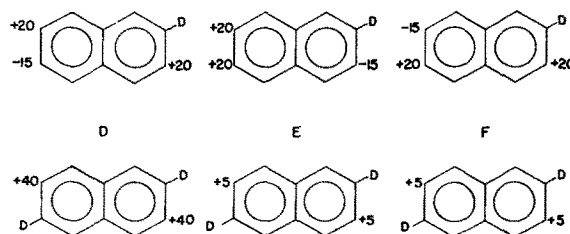

FIG. 4. Possible assignments of the experimental β-position proton hyperfine splittings in the naphthalene-2-d anion radical (upper structural formulas) and the corresponding predicted splittings for the naphthalene-2,6-d_2 anion (lower structural formulas) assuming an additivity relationship. Numbers are approximate deviations of the splittings from the undeuterated naphthalene anion in milligauss (see Table II). Assignment D is in agreement with the experimental data.

have been used where needed to resolve ambiguities in the assignments of splittings to position (see Table II).

The substitution of deuterium atoms in α positions causes the β-proton splittings to increase slightly, and vice versa (an effect of the second type), but in all cases no differences were resolved among the four protons of the unsubstituted set. Spectrum simulation[29] indicates that for many combinations of splitting constants a spread of values within the set of four protons of up to 20 mG would not have caused a marked difference in the spectra. The effect of α substitution on the β-proton splittings is 4.3, 5.1, 9.5, and 10.3 mG, respectively, for the mono-, di-, tri-, and tetra-substituted radicals studied, while β substitution causes the α-proton splittings to increase by 2.5, 3.8, and 10.5 mG, respectively, for the mono-, di-, and tetra-substituted compounds. The 2–4-mG changes for the mono-substituted anions are so small that they are within experimental error, but the over-all trend is clear; there is again approximate additivity with an increase of about 2–3 mG per substituted deuterium atom.

B. The a^H/a^D and Q_{CH}^H/Q_{CD}^D Ratios; Spin-Density Conservation

The ratio of the proton splittings at the α and β positions in the N^- radical is

$$(a_1^H/a_2^H) = 2.7066 \pm 0.0018,$$

while the corresponding ratio in N^--d_8 is

$$(a_1^D/a_2^D) = 2.656 \pm 0.006.$$

The same data can also be expressed as the ratios of the proton to the deuteron splittings at the α and β positions:

$$(a^H/a^D)_\alpha = 6.451 \pm 0.004,$$

and

$$(a^H/a^D)_\beta = 6.334 \pm 0.013,$$

FIG. 3. Possible assignments of the experimental α-position proton hyperfine splittings in the naphthalene-1-d anion radical (upper structural formulas) and the corresponding predicted splittings for the naphthalene-1,4-d_2 anion (lower structural formulas) assuming an additivity relationship. Numbers are approximate deviations of the splittings from the undeuterated naphthalene anion in milligauss (see Table II). Assignment A is in agreement with the experimental data.

[29] M. Kaplan, thesis, Columbia University, New York, 1965.

TABLE III. Equivalent total extent of spectra.

Deuterionaphthalene anion	Equivalent total extent of spectrum, Σa^H (G)[a]	Difference from N$^-$ $[\Sigma a^H - (\Sigma a^H)_{N^-}]$ (G)[b]
N$^-$-1-d	27.0749±0.0065	+0.0125±0.0098
N$^-$-2-d	27.0617±0.0130	−0.0007±0.0150
N$^-$-1,4-d_2	27.0686±0.0160	+0.0062±0.0176
N$^-$-2,6-d_2	27.0582±0.0102	−0.0042±0.0126
N$^-$-1,4,5-d_3	27.0941±0.0160	+0.0317±0.0176
N$^-$-1,4,5,8-d_4	27.0748±0.0178	+0.0124±0.0193
N$^-$-2,3,6,7-d_4	27.0544±0.0231	−0.0080±0.0242
N$^-$-1,2,3,6,7-d_5	27.0501±0.0195	−0.0123±0.0209
N$^-$-1,2,3,4,6,7-d_6	27.0958±0.0220	+0.0334±0.0232

[a] Σa^H is the sum of the proton splittings plus the sum of the deuteron splittings, the latter converted to equivalent proton splittings by using $a_\alpha^H = (6.451 \pm 0.004)a_\alpha^D$ and $a_\beta^H = (6.334 \pm 0.013)a_\beta^D$ for the α and β positions, respectively. The data are taken from Table II. Errors are based on those in Table II and in the a^H/a^D conversion factors.

[b] $(\Sigma a^H)_{N^-} = 27.0624 \pm 0.0074$ G.

respectively.[30] The κ values are [cf. Eq. (2)]

$$\kappa_\alpha = 0.9903 \pm 0.0007,$$

$$\kappa_\beta = 0.9724 \pm 0.0020.$$

There are two features of this isotope effect which require analysis: first, that κ_α and κ_β are both different from unity; and second, that κ_α and κ_β are different from each other. It is convenient to introduce a modified McConnell relationship[31] in which the spin densities ρ_i^H and ρ_i^D at the proton or deuteron attached to carbon atom i with pi-electron spin density ρ_i^π are employed instead of the hyperfine splittings a_i^H or a_i^D, respectively, i.e.,

$$\rho_i^H = q_{CH}^H \rho_i^\pi,$$

$$\rho_i^D = q_{CD}^D \rho_i^\pi. \tag{3}$$

The observed effects could result either from variation in the q's or the ρ_i^π's as a consequence of isotopic substitution. Upper limits to the difference between $(a^H/a^D)_\alpha$ and $(a^H/a^D)_\beta$ that could be produced by the variation in ρ_i^π as a result of isotopic substitution can be estimated from the measurements on the N$^-$-1,4,5,8-d_4 and N$^-$-2,3,6,7-d_4 anions (Table II) together with the assumption that the differences between the proton splittings in the various deuterated compounds and N$^-$ itself are caused solely by spin-density changes (see Sec. V). Such effects are clearly at least an order of magnitude too small to account for

the observations. The anomalous ratios must therefore be the result of variations in the effective q with position and with isotopic substitution, i.e., $(q_{CH}^H)_\alpha$, $(q_{CH}^H)_\beta$, $(q_{CD}^D)_\alpha$, and $(q_{CD}^D)_\beta$ must all have different values. Unfortunately, the form of the data does not permit the evaluation of these small differences with any degree of certainty.

An alternative method of examining the consistency of an explanation based on changes in the q's is to calculate the total spin density in the four α and four β positions. This can be done by first converting the deuteron splittings to equivalent proton splittings, and then comparing the sum of the equivalent proton splittings to the sum of the proton splittings in N$^-$. For any α-substituted deuterium atom, we take $a_\alpha^H = 6.451 \pm 0.004) a_\alpha^D$ as the equivalent proton splitting, and similarly, for any β-substituted deuterium atom, $a_\beta^H = (6.334 \pm 0.013) a_\beta^D$, i.e., we use the N$^-$ and N$^-$-d_8 radicals to determine the a^H/a^D ratios and assume that while the ratios are different for the α and β positions, they are the same for each type of substitution in all the deuterionaphthalenes. The results are shown in Table III, and the departures from the value of $\sum a_i^H$ for N$^-$ are all comparable to or less than the experimental errors. The largest discrepancy is $(0.12 \pm 0.09)\%$, and corresponds to a spin-density change for the γ (9, 10) positions of 0.001 units. Thus, within the accuracy of the data, there is no evidence for a shift of spin density from the α and β positions to the γ positions, and a high degree of consistency results from a model based on q variations.

V. DISCUSSION

In this section, we consider first the possible causes of the deviation of the a^H/a^D ratio from the expected values of 6.514, and then treat the influence of deuteration on the splittings at unsubstituted positions. Both isotope effects must result from the difference in mass of the proton and deuteron, and this difference can be manifested only through the molecular vibrations. As mentioned in the previous section, the vibrations can affect the sigma–pi coupling, the pi-electron spin-density distribution, or both.

A. The Anomalous a^H/a^D Ratio

The considerations at the end of the preceding section indicate that the anomalous a^H/a^D ratios arise from changes in q induced by the substitution of deuterium for hydrogen rather than from alterations in the spin density. We consequently examine the effects of molecular vibrations on q.

If orbital following is ignored, the out-of-plane C–H bending motions cause a significant direct overlap with the proton of the carbon-atom $2p$–π orbital containing the unpaired electron,[32] and this overlap gives rise to

[30] In obtaining the a^H/a^D ratios, data from the spectrum of N$^-$-d_8 containing N$^-$ were employed.

[31] H. M. McConnell, J. Chem. Phys. **24**, 633, 764 (1956); H. M. McConnell and H. H. Dearman, *ibid.* **28**, 51 (1958); H. M. McConnell and D. B. Chesnut, *ibid.* **28**, 107 (1958).

[32] B. Venkataraman and G. K. Fraenkel, J. Chem. Phys. **24**, 737 (1956).

a small positive contribution to q. Since the main part of q, which is a consequence of sigma–pi interaction, is negative, the vibrational motion causes a decrease in its over-all magnitude. The vibrational contribution is smaller for C–D bonds than for C–H bonds because the amplitude of the bending motion is less for the former than for the latter and, accordingly, $|q_{CD}{}^D|$ is predicted to be larger than $|q_{CH}{}^H|$, and κ should be less than unity. Unfortunately, the vibrational effects are considerably more complicated than assumed in this simple qualitative model, and it is difficult to make the arguments quantitative. In a careful study of the methyl radical, Schrader and Karplus[33] found that the vibrational motion affects the indirect sigma-pi interaction as well as the direct overlap, and that the degree to which the orbitals follow the bending motion strongly influences the magnitude of the direct overlap. Because of uncertainties in certain integrals, it was not possible, in this investigation, to obtain a realiable *a priori* estimate for the a^H/a^D ratio. A detailed evaluation of the a^H/a^D ratio will thus have to await a resolution of the questions concerning the magnitude of the contributions to q from the out-of-plane bending motions, and even once these are known, application to naphthalene will require appropriate averaging over the normal modes of N^- and its deuterated analogs.

Although a quantitative treatment along the lines outlined should yield values of κ less than unity and of approximately the correct magnitude, it might not fully account for the difference in the a^H/a^D ratio at the α and β positions. There is, however, an additional effect which has recently been emphasized by Moss[34]: When, as the result of the vibrational motion, the proton is out of the plane of the aromatic system, the pi-electron spin density on a carbon atom which is adjacent to the carbon atom bonded to the proton causes a positive spin polarization at the proton. The mechanism invoked to cause this polarization for the out-of-plane protons is similar to the one which produces splittings in methyl-group substituents.[35–37] The spin-density distribution in the naphthalene anion is such that contributions of this sort should be much larger at the β position that at the α position, and the effect is expected to be larger for proton than for deuteron splittings because of the smaller vibrational contribution to the latter. As a result, the value of κ should be smaller at the β position than at the α position, in agreement with the experimental observations. Quantitative evaluation of this effect requires averaging over the normal modes. This does not appear to be worthwhile at present, particularly because Moss' formula gives unreasonable results for the β position in naphthalene.

B. Variations of Splittings at Unsubstituted Positions

The influence of deuterium substitution on the splittings at positions other than the one which is deuterated could result either from changes in the sigma-pi interaction parameters (q's) or from changes in the spin densities. Alteration of the value of q at one position by substitution at another would have to be a consequence of distortion of the normal modes by deuteration. Since, however, the dependence of q on vibrations involves a *summation* over all of the out-of-plane modes, this effect of deuteration is, to a very good approximation, limited to the position of substitution.[38] By contrast, local structural perturbations can produce significant spin-density changes throughout the molecule. The simplest phenomenological way of describing these perturbations is through alterations of the pi-electron parameters, as for example, the Coulomb integral α_r or the resonance integral β_{rs}, and in a previous note[39] a model for the vibrational perturbation of the resonance integral was described as a means of explaining the nonlocal effects of deuteration in the benzene and cyclooctatetraene anions. Here we apply this model to the deuterated naphthalene radicals. Since comparative reaction-rate and equilibrium data for deuterated and undeuterated aromatic compounds has generally been interpreted by regarding deuterium as a weakly electron-donating substituent,[40] we also consider this alternative and contrast the results of a Coulomb-integral perturbation with those obtained from the resonance-integral perturbation.

We use Hückel molecular-orbital theory and assume that the carbon-atom skeleton is fixed so that only the hydrogen or deuterium atoms undergo vibrations. If the carbon-atom $2p$–π orbitals follow the out-of-plane bending motions of the C–H or C–D bonds, the overlap integral, and therefore also the resonance integral, between neighboring C–C bonds should decrease as the amplitude of the vibrational motion increases. The effective magnitude of β to be used in the calculation of the electronic wavefunctions is thus expected to be smaller for carbon atoms bonded to hydrogen atoms than when one or more of the hydrogens are replaced by deuterium atoms. The effective resonance integral $\beta_{r,r\pm1}$ between the deuterium-substituted carbon atom (r) and those contiguous to it ($r\pm1$) can thus be written as

$$\beta_{r,r\pm1} = (1 + \delta^{(\beta)}{}_{r,r\pm1})\beta_0, \qquad (4)$$

where β_0, the carbon–carbon resonance integral in a

[33] D. M. Schrader and M. Karplus, J. Chem. Phys. **40**, 1593 (1964).

[34] R. E. Moss, Mol. Phys. **10**, 339 (1966).

[35] R. Bersohn, J. Chem. Phys. **24**, 1066 (1956).

[36] D. B. Chesnut, J. Chem. Phys. **29**, 43 (1958).

[37] A. D. McLachlan, Mol. Phys. **1**, 233 (1958).

[38] Calculations of this effect in neutral benzene have been performed by D. L. Purins. In benzene, the expectation value of the square of the out-of-plane bending angle of the C–H$_i$ bond, when summed over all the normal modes, is $\langle \phi_i{}^2 \rangle = 0.02645$. In benzene-$d_1$, $\langle \phi_1{}^2 \rangle = 0.02217$, while $\langle \phi_2{}^2 \rangle = 0.02640$, $\langle \phi_3{}^2 \rangle = 0.02645$, and $\langle \phi_4{}^2 \rangle = 0.02645$.

[39] M. Karplus, R. G. Lawler, and G. K. Fraenkel, J. Am. Chem. Soc. **87**, 5260 (1965).

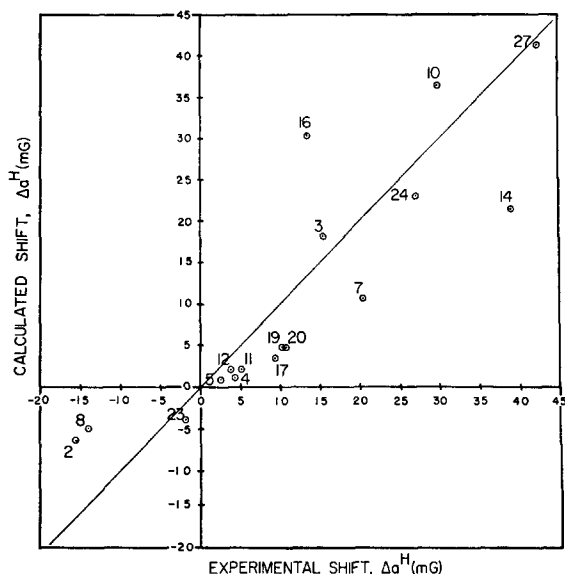[40] E. A. Halevi, Progr. Phys. Org. Chem. **1**, 109 (1963).

FIG. 5. Plot of calculated vs experimental deviations Δa^H (milligauss) of the proton hyperfine splittings of the deuterio-naphthalene anion radicals from those of the undeuterated naphthalene anion using the resonance-integral perturbation model $\delta_{rs}^{(\beta)}$ to account for the effect of deuterium substitution. The calculations were made with $\delta_{12}^{(\beta)}=0.004$. The straight line is of unit slope and corresponds to perfect correlation. Numbers next to the points refer to the last column of Table IV.

normal aromatic framework, already includes a vibrational averaging. The difference in the vibrational averaging for deuterium-substituted and unsubstituted positions is represented by $\delta^{(\beta)}_{r,r\pm1}$ and, as indicated, it should be a positive quantity, i.e., $|\beta_{r,r\pm1}|$ is greater than $|\beta_0|$. Since the effects are small, a perturbation procedure is sufficiently accurate, and substitution at more than one position is just the sum of the effects of single substitutions, in agreement with the experimentally observed additivity relationship (Sec. IV). Making use of the standard Hückel-theory perturbation formulas,[41] the change in energy of the kth level is readily shown to be (in units of β_0)

$$\Delta E_k = 2 \sum_r c_r^{(k)} [\delta^{(\beta)}_{r,r-1} c^{(k)}_{r-1} + \delta^{(\beta)}_{r,r+1} c^{(k)}_{r+1}], \quad (5)$$

where the summation is over all substituted positions, and $c_r^{(k)}$ is the coefficient of the $2p-\pi$ carbon orbital at position r in the kth wavefunction (with energy E_k). Similarly, the change in spin density at position s is

$$\Delta\rho_s^{\pi} = 2c_s^{(n)} \sum_r \sum_m {}'\{[\delta^{(\beta)}_{r,r-1}(c_r^{(m)}c_{r-1}^{(n)} + c_r^{(n)}c_{r-1}^{(m)})$$
$$+ \delta^{(\beta)}_{r,r+1}(c_r^{(m)}c_{r+1}^{(n)} + c_r^{(n)}c_{r+1}^{(m)})]$$
$$\times (E_n - E_m)^{-1}\}c_s^{(m)} \quad (6a)$$

$$= \tfrac{1}{2} \sum_r (\delta^{(\beta)}_{r,r-1}\pi^{(n)}_{s;r,r-1} + \delta^{(\beta)}_{r,r+1}\pi^{(n)}_{s;r,r+1}), \quad (6b)$$

[41] C. A. Coulson and H. C. Longuet-Higgins, Proc. Roy. Soc. (London) **A191**, 39 (1947).

where the orbital containing the unpaired electron is designated by n, the prime on the summation over m in Eq. (6a) indicates that all energy levels (with coefficients $c_i^{(m)}$ and energies E_m) are included except the one occupied by the unpaired electron $(m \neq n)$, and the energies are in units of β_0. The quantity $\pi^{(n)}_{s;rt}$ is the contribution from the nth orbital to the mutual polarizability of atom s and bond $r-t$; it is defined here by Eqs. (6a) and (6b).

The alternative procedure is to introduce an electron-donating effect by assuming that the Coulomb integral at the substituted positions is slightly changed; i.e., for the substitution of a deuterium atom at position r, we let

$$\alpha_r = \alpha + \delta_r^{(\alpha)}\beta_0, \quad (7)$$

where α is the Coulomb integral at an unsubstituted position and, as above, β_0 is the usual carbon–carbon resonance integral. The parameter $\delta_r^{(\alpha)}$ is negative for an electron-donating effect. Again using perturbation-theory,[41] we find, in the notation used above, that

$$\Delta E_k = \sum_r \delta_r^{(\alpha)}(c_r^{(k)})^2, \quad (8)$$

and

$$\Delta\rho_s^{\pi} = 2c_s^{(n)} \sum_r \sum_m {}' \delta_r^{(\alpha)}[(c_r^{(m)}c_r^{(n)})/(E_n - E_m)]c_s^{(m)}, \quad (9a)$$

$$= \tfrac{1}{2} \sum_r \delta_r^{(\alpha)}\pi_{sr}^{(n)}, \quad (9b)$$

where $\pi_{sr}^{(n)}$ is the contribution of the nth orbital to the mutual polarizability of atoms r and s, and is defined here by Eqs. (9a) and (9b). As above, the energies are in units of β_0.

In a radical with inequivalent positions (like the naphthalene negative ion), the magnitudes of the resonance- and Coulomb-integral perturbations may be functions of position because both depend on the details of the vibrational wavefunctions. The variations are not, however, expected to be very great, and they are neglected in the heuristic calculations carried out below. In this approximation, the resonance-integral perturbation β_{rs} for the common bond between two adjacent carbon atoms that are both substituted with deuterium atoms is altered by $2\delta_{rs}^{(\beta)}$.

1. Results of the Resonance-Integral Perturbations in the Naphthalene Anions

If a single value of $\delta_{rs}^{(\beta)}$ is valid for all positions in the deuterated naphthalene anions, Eq. (6b) together with McConnell's relation show that the experimental changes in hyperfine splitting at position s, $\Delta |a_s^H| = |Q_{CH}^H| \Delta\rho_s^{\pi}$, should give a straight line of slope $(\tfrac{1}{2}) |Q_{CH}^H| \delta_{12}^{(\beta)}$ when plotted against $\sum_r(\pi^{(n)}_{s;r,r-1} + \pi^{(n)}_{s;r,r+1})$. General agreement is found for the data from all the positions in all the radicals studied both with respect to the signs and magnitudes of the $\Delta |a_s^H|$.

TABLE IV. Calculated changes in hyperfine splittings on deuteration.

Deuterionaphthalene anion	Position	Coulomb-integral perturbation $(\delta_1^{(\alpha)} = -0.0076)$	Average	Resonance-integral perturbation $(\delta_{12}^{(\beta)} = 0.004)$	Average	Exptl.	Position in Fig. 5
		Hyperfine splitting relative to naphthalene (milligauss).[a]					
N⁻-1-d	1	[− 4.9]	[− 4.9]	[−34.8]	[−34.8]	[−20.1]	1
	4	−20.6	−20.6	− 6.4	− 6.4	−15.6	2
	5	13.7⎫	17.3	15.9⎫	18.2	15.5	3
	8	20.8⎭		20.4⎭			
	2	−20.8⎫		−10.8⎫			
	3	4.8⎪	− 2.3	5.8⎪	1.2	4.3	4
	6	9.2⎪		8.6⎪			
	7	− 2.3⎭		1.2⎭			
N⁻-2-d	1	−20.8⎫		−10.7⎫			
	4	4.8⎪	− 2.3	5.7⎪	1.1	2.5	5
	5	9.2⎪		8.5⎪			
	8	− 2.3⎭		1.1⎭			
	2	[−11.9]	[−11.9]	[−21.2]	[−21.2]	[−36.6]	6
	3	20.8⎫	15.0	14.4⎫	10.7	20.4	7
	7	9.3⎭		7.0⎭			
	6	− 9.2	− 9.2	− 4.9	− 4.9	−14.9	8
N⁻-1,4-d₂	1, 4	[−25.5]	[−25.5]	[−41.2]	[−41.2]	[−36.9]	9
	5, 8	34.6	34.6	36.4	36.4	29.8	10
	2, 3	−16.0⎫	− 4.5	− 5.1⎫	2.3	5.1	11
	6, 7	6.9⎭		9.8⎭			
N⁻-2,6-d₂	1, 5	−11.7⎫	− 4.6	− 2.3⎫	− 2.2	3.8	12
	4, 8	2.4⎭		6.7⎭			
	2, 6	[−21.0]	[−21.0]	[−26.0]	[−26.0]	[−48.6]	13
	3, 7	30.2	30.2	21.4	21.4	38.9	14
N⁻-1,4,5-d₃	1	[−11.7]⎫		[−25.3]⎫			
	4	[− 4.7]⎬	[4.5]	[−20.8]⎬	[−14.9]	[− 6.6]	15
	5	[29.8]⎭		[1.4]⎭			
	8	14.0	14.0	30.4	30.4	13.5	16
	2	− 6.9⎫		3.6⎫			
	3	−18.3⎪	− 6.9	− 3.9⎪	3.6	9.5	17
	6	−14.0⎪		− 1.1⎪			
	7	11.7⎭		15.8⎭			
N⁻-1,4,5,8-d₄	1, 4, 5, 8	[9.2]	[9.2]	[− 4.8]	[− 4.8]	[− 7.2]	18
	2, 3, 6, 7	− 9.2	− 9.2	4.8	4.8	10.3	19
N⁻-2,3,6,7-d₄	1, 4, 5, 8	− 9.2	− 9.2	4.8	4.8	10.5	20
	2, 3, 6, 7	[9.2]	[9.2]	[− 4.8]	[− 4.8]	[−12.5]	21
N⁻-1,2,3,6,7-d₆	1	[−14.0]	[−14.0]	[−29.9]	[−29.9]	[−15.0]	22
	4	−29.9	−29.9	− 1.8	− 1.8	− 3.9	23
	5	4.5⎫	8.1	20.6⎫	23.0	27.1	24
	8	11.7⎭		25.4⎭			
	2	[−11.6]⎫		[−15.2]⎫			
	3	[13.9]⎪	[6.9]	[0.6]⎪	[− 3.6]	[−11.9]	25
	6	[18.4]⎪		[3.9]⎪			
	7	[6.9]⎭		[− 3.6]⎭			
N⁻-1,2,3,4,6,7-d₆	1, 4	[−34.7]	[−34.7]	[−36.4]	[−36.4]	[−22.1]	26
	5, 8	25.4	25.4	41.3	41.3	42.2	27
	2, 3	[− 6.9]⎫	[4.6]	[− 9.9]⎫	[− 2.4]	[− 1.7]	28
	6, 7	[16.1]⎭		[5.0]⎭			

[a] Splittings are calculated from spin densities using $|Q_{CH}^H| = 27.0$ G. Values in brackets are for deuterated positions but are expressed as equivalent proton splittings. The experimental values given for the α- and β- deuterated positions were obtained by using the conversion factors $(a_\alpha^H/a_\alpha^D) = 6.451$ and $(a_\beta^H/a_\beta^D) = 6.334$ and the data from Table II.

The calculated changes in splittings with a fitted value of $\delta_{12}^{(\beta)} \cong 0.004$, which is comparable to that estimated for the benzene negative ion[39] $(\delta_{12}^{(\beta)} \cong 0.0025)$, are given in Table IV, and the calculated changes are plotted against the experimental changes in Fig. 5. Positions that are predicted to have different splittings but which were observed to be the same have been calculated by averaging their computed values, as indicated in the table. The greatest spread of calculated values averaged in this way was only about 20 mG, and spectrum simulation indicates that this spread of the splittings would not have been resolvable.

The over-all agreement is seen to be quite good for all protons at positions of both the first and second types (Sec. IV), i.e., those that are within the substituted set as well as those that are in the unsubstituted set. Even though the experimental data for the deuterium splittings is of relatively low accuracy, calculations for the substituted positions also yield satisfactory agreement. Since discrepancies that do exist show trends that are correlated with the position involved, the results might be improved if the variation of the value of $\delta_{rs}{}^{(\beta)}$ with bond type were included in the calculations. A refinement such as this, however, would require averaging over the molecular vibrations, a procedure which is beyond the scope of the present analysis.

2. Result of the Coulomb-Integral Perturbations in the Naphthalene Anions

In a manner analogous to the treatment carried out for the resonance-integral perturbation, a plot of $\Delta \mid a_s{}^{H} \mid$ versus $\sum_r \pi_{rs}{}^{(n)}$ should give a straight line of slope $(\frac{1}{2}) \mid Q_{CH}{}^{H} \mid \delta_1{}^{(\alpha)}$ if Eq. (9b) with one value of $\delta_r{}^{(\alpha)}$ is a valid approximation. A plot of this kind shows good agreement for effects of the first type (Sec. IV), but not for effects of the second type. The results obtained with a fitted value of $\delta_1{}^{(\alpha)} = -0.0076$ are given in Table IV, and although it can be seen that the 4, 5 and 8 positions of N^{-}-1-d are in good agreement with experiment, the average for the β positions is predicted to have a change of the wrong sign. This discrepancy for the effects of the second type is shown more clearly for the N^{-}-1,4,5,8-d_4 and N^{-}-2,3,6,7-d_4 radicals for which the predicted changes in proton splittings are about -9 mG as compared to an observed change of about 10 mG. The other radicals show a corresponding behavior.

Values in the table for positions predicted to have different splittings but which were observed to have the same splitting have been averaged in the same way as for the resonance-integral perturbation. The largest spread of calculated values which had to be averaged was about 11 mG for positions within the substituted set (first type), while for the unsubstituted set (second type) the largest range was about 30 mG. The former would not have been resolved in our experiments, but spectrum simulation indicates that some line distortion might be barely detectable in some of the radicals when there is a spread of 30 mG.

The negative sign found for $\delta_1{}^{(\alpha)}$ is consistent with the anticipated electron-donating influence of deuterium (lower effective electronegativity than hydrogen), and the magnitude of $\delta_1{}^{(\alpha)}$ is a factor of ten smaller than the magnitude used in inductive-model calculations for the methyl group in the toluene anion radical,[42]

as would be expected for a very weak electron-donating effect. The straight line corresponding to the best fit in the plot of $\Delta \mid a_s{}^{H} \mid$ versus $\sum_r \pi_{sr}{}^{(n)}$ for positions of the first type passes close to the origin. This would be a necessary result if the inductive model alone were sufficient to account for the changes caused by deuterium substitution. Essentially, similar spin densities are found by the approximate configuration–interaction procedure of McLachlan,[43] except that in the plot of $\Delta \mid a_s{}^{H} \mid$ versus $\sum_r \pi_{sr}{}^{(n)}$, the slope $(\frac{1}{2} \mid Q_{CH}{}^{H} \mid \delta_1{}^{(\alpha)})$ is now somewhat smaller in magnitude. Both the Hückel and McLachlan calculations give identical spin-density distributions for the N^{-} and N^{-}-d_8 radicals.

A calculation using Eq. (9) can also be applied to the methyl-substituted naphthalene negative ions studied by several investigators.[44-49] Although certain discrepancies exist, the ring-proton splittings are on the whole in agreement[45,46,49] with the calculations for positions that are both within the substituted set and also for those not in the substituted set (effects of both the first and second types). Thus, there does not appear to be anything intrinsically wrong about a Hückel inductive-type calculation for weakly electron-donating substituents, and the discrepancies found for the deuterionaphthalenes cannot justifiably be attributed to inadequacies in the nature of the approximations in the basic molecular-orbital theory.

3. Comparison of the Resonance- and Coulomb-Integral Perturbations

The rather good agreement with experiment obtained from the calculations using the resonance-integral perturbation model for all the compounds, and the striking disagreement found in certain cases for the Coulomb-integral perturbation, confirm the conclusions drawn previously[39] in the interpretation of the $C_6H_5D^{-}$ and $C_8H_7D^{-}$ ESR spectra: Any Coulomb-integral perturbation introduced by deuterium substitution must have a considerably smaller effect on the hyperfine splittings of aromatic anions than does the resonance-integral perturbation.

To clarify the difference between the resonance and Coulomb integral perturbations, it is helpful to consider the radical N^{-}-1,4,5,8-d_4 in some detail. Since both perturbations in this case are totally symmetric with respect to the symmetry group of naphthalene (D_{2h}), only orbitals that belong to the same irreducible

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[49] R. E. Moss, N. A. Ashford, R. G. Lawler, and G. K. Fraenkel (unpublished).

representation of naphthalene interact. The unpaired electron is in a B_{2g} orbital

$$\psi_6 = -c_2(\phi_1+\phi_4-\phi_5-\phi_8)+c_1(\phi_2+\phi_3-\phi_6-\phi_7),$$

$$E_6 = -k, \tag{10a}$$

which interacts with the one other B_{2g} orbital

$$\psi_2 = c_1(\phi_1+\phi_4-\phi_5-\phi_8)+c_2(\phi_2+\phi_3-\phi_6-\phi_7),$$

$$E_2 = (1+k), \tag{10b}$$

where $c_1=0.2629$, $c_2=0.4253$, and $k=0.618$ in the Hückel approximation and, as follows directly from the secular equation for naphthalene, $c_1^2-c_2^2+c_1c_2=0$. Substituting into Eqs. (6) and (9) and making use of the relations between the coefficients, we obtain for the Coulomb-integral perturbation

$$\Delta\rho_\alpha^\pi = -\Delta\rho_\beta^\pi = -(8\delta_1^{(\alpha)}c_1^2c_2^2)/(1+2k), \tag{11}$$

and for the resonance-integral perturbation

$$\Delta\rho_\alpha^\pi = -\Delta\rho_\beta^\pi = -(8\delta_{12}^{(\beta)}c_1^2c_2^2)/(1+2k). \tag{12}$$

Thus we find that on substitution the shifts in spin density for a negative $\delta_1^{(\alpha)}$ and a positive $\delta_{12}^{(\beta)}$ perturbation are in opposite directions. Since k is positive, we have from the Coulomb-integral perturbation $\Delta\rho_\beta^\pi<0$ and $\Delta\rho_\alpha^\pi>0$, while from the resonance-integral perturbation, we have $\Delta\rho_\beta^\pi>0$ and $\Delta\rho_\alpha^\pi<0$. The result for the resonance-integral perturbation is in agreement with experiment (see Table IV). For the $N^--2,3,6,7-d_4$ ion, the spin-density changes are again given by Eqs. (11) and (12), except that all signs are changed. The resonance-integral perturbation thus gives the results $\Delta\rho_\alpha^\pi>0$ and $\Delta\rho_\beta^\pi<0$, which again are in agreement with experiment. That the $N^--2,3,6,7-d_4$ and $N^--1,4,5,8-d_4$ ions have corresponding formulas for the spin-density shifts for the resonance-integral perturbation may appear surprising. The relationship arises because the contribution from the 2,3 and 6,7 bonds in $N^--2,3,6,7-d_4$ is twice as large $(\delta_{23}^{(\beta)}=2\delta_{12}^{(\beta)}$ in this case) as the contribution from the $(1,2)$, $(3,4)$, $(5,6)$, and $(7,8)$ bonds, but of opposite sign.

The preponderance of the β-perturbation over the Coulomb-integral perturbation raises important questions with respect to the thermodynamic and kinetic studies because these investigations have been interpreted by assuming that deuterium is an electron-donating substituent.[40] It appears, however, that no attempt has been made to use a Coulomb-integral perturbation to explain the inductive character of secondary deuterium isotope effects in aromatic systems. Instead, "direct" field-effect models based on the difference between the C–H and C–D bond moments have been employed. Nevertheless, we can inquire into the limits on $\delta_r^{(\alpha)}$ set by the ESR measurements by considering the Hammett σ values for meta

substitution of a methyl group[50] and a deuterium atom.[51] They are $\sigma_{meta}=-0.069$ for CH_3 and $\sigma_{meta}=-0.0012$ for D. Since the ratio $[\sigma_{meta}(D)/\sigma_{meta}(CH_3)]\cong0.017$, should be comparable to the ratio of the $\delta^{(\alpha)}$ values, and $\delta^{(\alpha)}$ for methyl substitution has been estimated to be $\delta^{(\alpha)}\sim-0.1$ in the toluene anion radical,[42] a value of $\delta^{(\alpha)}\sim-0.0017$ would appear to be needed for deuterium in order to account for kinetic isotope effects of the observed magnitude. A Coulomb-integral perturbation as small as this would probably not produce a significant effect on the ESR spectra. Despite the crude nature of these arguments, they suggest that the present experiments, and their interpretation in terms of a resonance-integral perturbation, are not inconsistent with an inductive contribution to the secondary deuterium isotope effects in aromatic systems.

The kinetic systems are quite complex and it is perhaps not surprising that some exploratory Hückel calculations which we performed using both the resonance- and Coulomb-integral perturbations did not yield any straightforward correlation with the limited data[40,52] available. It is thus clear that the ESR measurements provide a more direct means of studying the vibrational perturbations than do kinetic studies.

ACKNOWLEDGMENTS

APPENDIX

In the determination of the relative g values of the naphthalene and deuterated naphthalene negative ions (see Sec. III), some inconsistencies were observed and therefore certain lines in the spectrum obtained from a mixture of the naphthalene (N^-) and per-deuterionaphthalene ($N^- - d_8$) anions were remeasured. Since the second-order shifts[21,25] affect the g-value determination, a detailed numerical analysis of their contribution was also carried out, and it was found that the usual assumptions employed in this sort of treatment were unsuitable. We report on these investigations, and also on a spectrum of N^- which had especially narrow lines, in this Appendix.

It can be shown[21,25,53] that the appropriate representation for the description of the components of a degenerate hyperfine line is based on the total angular-

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TABLE V. Naphthalene (N⁻) and perdeuterionaphthalene (N⁻-d_8) anions. Accurate measurements of line positions and spectrum centers.

Radical anion	Spectral index numbers[a] M_α, M_β	Line position[b] ν_p (kc/sec)	Spectrum center[b,c] ν_p^0 (kc/sec)
N⁻	$\bar{2}, 0$	13 919.957	13 962.025
	2, 0	14 004.093	
	$\bar{1}, \bar{1}$	13 933.238	13 962.042
	1, 1	13 990.846	
	$\bar{1}, 0$	13 941.009	13 962.042
	1, 0	13 983.075	
	$\bar{1}, 1$	13 948.777	13 962.040
	1, $\bar{1}$	13 975.303	
N⁻-d_8	$\bar{1}, \bar{1}$	13 957.560	13 962.050
	1, 1	13 966.540	
	$\bar{1}, 0$	13 958.786	13 962.050
	1, 0	13 965.314	
	0, $\bar{1}$	13 960.824	13 962.050₅
	0, 1	13 963.277	

[a] See Ref. 23. The quantum numbers M_α and M_β refer to the total field-direction component of the α- and β-proton nuclear-spin angular momenta, respectively ($M_\alpha = \Sigma_\alpha m_i$, $M_\beta = \Sigma_\beta m_i$).

[b] Frequencies are those of the proton NMR Larmor frequency normalized to a microwave frequency of 9191.900000 Mc/sec. The average deviations from the mean based on at least five measurements of line positions was 1-2 cps for all lines. The widths of all the lines were about 20 mG.

[c] Mean proton resonance frequency of the pair of lines in the adjacent column.

momentum quantum numbers J for each set of equivalent nuclei provided that certain types of intramolecular line-broadening effects are not too large. This quantum number determines the eigenvalues $J(J+1)$ of the operator $\mathbf{J}^2$ (in units of $\hbar$), where $\mathbf{J} = \sum \mathbf{I}_i$ is the sum of the total nuclear-spin angular momenta $\mathbf{I}_i$ of the protons in each equivalent set. For the naphthalene negative ion, there are two equivalent sets each containing four protons (α and β), and there are two quantum numbers, J_α and J_β. Each can take on the values 0, 1 and 2, with degeneracies $D_J = 2, 3$ and 1, respectively. The second-order corrections to the line positions for the components with quantum numbers J_α, J_β of a line with quantum numbers M_α, M_β (and therefore with first-order positions $[M_\alpha a_\alpha + M_\beta a_\beta]$ relative to the center of the spectrum) are[21,25]

$$\Delta B(M_\alpha, J_\alpha; M_\beta, J_\beta) = -(2B_0)^{-1}\{a_\alpha^2[J_\alpha(J_\alpha+1) - M_\alpha^2]$$
$$+ a_\beta^2[J_\beta(J_\beta+1) - M_\beta^2]\}, \quad (A1)$$

where B_0 is the value of the external (Zeeman) magnetic field. When these shifts are too small to be resolved, the net shift is given by the average over the shifts for all the components of a degenerate line,[21,25] and for nuclei of spin $I = \frac{1}{2}$ this net shift is the same for

all lines. For the naphthalene negative ion the average shift is

$$\langle \Delta B \rangle = -(4B_0)^{-1}[n_\alpha a_\alpha^2 + n_\beta a_\beta^2] = -B_0^{-1}(a_\alpha^2 + a_\beta^2)$$
$$= -8.46 \text{ mG}, \quad (A2)$$

at a field of $B_0 = 3280$ G. The perdeuterionaphthalene anions will have shifts of the order of $(6.5)^2 \cong 42$ times less than this. Numerical values computed from Eq. (A1) are discussed below (see Table VII).

One spectrum of N⁻ had particularly sharp lines (see Sec. III) and it exhibited partially resolved second-order components in lines with quantum numbers $M_\alpha = 0$ and ± 1. The components with $J_\alpha = 2$ appear as a shoulder on the low-field side of the remaining components with $J_\alpha = 0$ and 1, so that all lines with $M_\alpha = 0$, ± 1 are markedly asymmetric. Those with $M_\alpha = \pm 2$ have a width of about 15 mG and are symmetric, as expected, since they are nondegenerate. When the microwave power was lowered, the apparent position of the smaller component of the $M_\alpha = 0$, ± 1 lines dropped to a lower point on the side of the main line. This occurred because the components with large values of J saturate less readily[53-57] than do those with

TABLE VI. Naphthalene (N⁻) and perdeuterionaphthalene (N⁻-d_8) anions. Line-position differences.

Radical anion	Line 1 $\tilde{M}_\alpha, \tilde{M}_\beta$	Line 2 $\tilde{M}_\alpha, \tilde{M}_\beta$	Corresponding splitting[b]	Frequency[b] $\Delta\nu_p = [\nu_p(1) - \nu_p(2)]$ (kc/sec)
N⁻	2, 0	$\bar{2}, 0$	$4a_\alpha^H$	84.136
	1, 0	$\bar{1}, 0$	$2a_\alpha^H$	42.066
	1, $\bar{1}$	$\bar{1}, \bar{1}$	$2a_\alpha^H$	42.065
	1, 1	$\bar{1}, 1$	$2a_\alpha^H$	42.069
	1, 1	1, 0	a_β^H	7.771
	1, 0	1, $\bar{1}$	a_β^H	7.772
	$\bar{1}, 1$	$\bar{1}, 0$	a_β^H	7.768
	$\bar{1}, 0$	$\bar{1}, \bar{1}$	a_β^H	7.771
N⁻-d_8	1, 0	$\bar{1}, 0$	$2a_\alpha^D$	6.528
	1, 1	0, 1	a_α^D	3.263
	0, $\bar{1}$	$\bar{1}, \bar{1}$	a_α^D	3.264
	0, 1	0, $\bar{1}$	$2a_\beta^D$	2.453
	1, 1	1, 0	a_β^D	1.226
	$\bar{1}, 0$	$\bar{1}, \bar{1}$	a_β^D	1.226

[a] See Footnote a, Table V.

[b] The splitting constant (or its multiple) as determined (to first order) by the difference in frequencies $\Delta\nu_p = \nu_p(1) - \nu_p(2)$, where Lines 1 and 2 have spectral-index numbers given in the preceding columns (in proton frequency units). Data from Table V.

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TABLE VII. Second-order shifts for the naphthalene negative ion.

Spectral index numbers[a] $\tilde{M}_\alpha, \tilde{M}_\beta$	Total ang. mom. quantum numbers[b] J_α, J_β	Degeneracy[c] $D_J = D_{J\alpha} \times D_{J\beta}$	$\delta=0$	$\delta=5$	$\delta=10$	$\delta=15$	$\delta=20$	$\delta=25$	$\delta=30$	$\delta=50$	$\delta=100$
				Computed second-order shifts, $-\Delta B$ (mG), as function of linewidths, δ[d]								
0, 0	0, 0	4	0								
	0, 1	6	1.02	0.6 (273)[e]							
	0, 2	2	3.06		5.0 (916)[e]	5.4 (999)[e]					
	1, 0	6	7.44	8.6 (534)[e]			7.2	8.4	8.5[f]	8.5[f]	8.5[f]
	1, 1	9	8.46								
	1, 2	3	10.50								
	2, 0	2	22.32	23.4 (193)[e]	24.1 (84)[e]	24.3 (1)[e]					
	2, 1	3	23.34								
	2, 2	1	25.38								
0, ±1	0, 1	6	0.51	g							
	0, 2	2	2.55	g							
	1, 1	9	7.95	g							
	1, 2	3	9.99	g							
	2, 1	3	22.83	g							
	2, 2	1	24.85	g							
0, ±2	0, 2	2	1.02	g							
	1, 2	3	8.46	g							
	2, 2	1	23.34	g							
±1, 0	1, 0	6	3.72	4.7 (771)[e]	4.6 (868)[e]	5.1 (949)[e]					
	1, 1	9	4.74				9.4	8.9	8.7	8.5[f]	8.5[f]
	1, 2	3	6.78								
	2, 0	2	18.60	19.7 (229)[e]	20.3 (132)[e]	20.1 (51)[e]					
	2, 1	3	19.62								
	2, 2	1	21.66								
±1, ±1	1, 1	9	4.23	4.7 (769)[e]	4.6 (866)[e]	5.0 (948)[e]					
	1, 2	3	6.27				9.4	8.9	8.7	8.5[f]	8.5[f]
	2, 1	3	19.11	19.7 (231)[e]	20.3 (133)[e]	20.2 (52)[e]					
	2, 2	1	21.15								
±1, ±2	1, 2	3	4.74	g							
	2, 2	1	19.62	g							
±2, 0	2, 0	2	7.44	g							
	2, 1	3	8.46	g							
	2, 2	1	10.50	g							
±2, ±1	2, 1	3	7.95	g							
	2, 2	1	9.99	g							
±2, ±2	2, 2	1	8.46	8.5[f]	8.5[f]	8.5[f]	8.5[f]	8.5[f]	8.5[f]	8.5[f]	8.5[f]

[a] See Table V, Footnote a.

[b] See text and Eq. (A1).

[c] Degeneracies D_J are $D_J=2$, 3, 1 for $J=0$, 1, 2, respectively; see text.

[d] Computed as described in text from Eq. (A1) and, for $\delta\neq0$, by spectrum simulation. Width δ is the separation between extrema of the first derivative of the spectrum of the individual components all of which are taken to be the same. The positions tabulated are those corresponding to the midpoint of the positions of the extrema of the first derivative of the spectrum.

[e] When more than one line is resolved for $\delta\neq0$, the relative amplitudes are listed in parentheses on a scale totaling to 1000 for each first-order line.

[f] The average shift is 8.46 mG, and is equal to the shift for the lines with $M_\alpha=2$, $M_\beta=2$ and $M_\alpha=-2$, $M_\beta\approx-2$. The spectrum-simulation program rounds this value to 8.5 mG.

[g] Second-order shifts not computed.

small values of J. The separation of the two highly overlapped components of the central line is about 20 mG. This value is in accord with the calculations given in the following for true linewidths of 10–15 mG.

Careful measurements were also made on a sample containing a mixture of N⁻ and N⁻-d_8 by simultaneously determining the microwave and proton-resonance frequencies at the centers of several lines. Special pro-

cedures had to be employed in performing these measurements so as to eliminate certain undesirable characteristics of the magnetic field. In the typical experimental arrangements we have employed, the difference between the magnetic field at the sample and at the proton probe located just outside the microwave cavity of the spectrometer is about 50 to 100 mG. Although this difference does not introduce any significant errors

in the determination of relative line positions, recent investigations[26] have shown that its magnitude is a function of the past history of the magnet, and unless a carefully controlled procedure is employed, the field difference may vary between the measurement of one line and another. Faber[58] has developed a routine for minimizing this difficulty: The field is first scanned several times in both directions over a range sufficient to traverse the entire extent of the part of the spectrum to be measured. The first line on the low-field side is then approached taking care not to overshoot its position, and its center is located by adjusting the field over as small a range as possible (no more than a few hundred milligauss). The next line is then approached in a similar manner, and so on. The entire sequence of measurements is repeated by starting on the high-field side. In measuring the line positions, the center of each line was taken to be the point halfway between the first-derivative extrema. Positions measured in this way are not the same as those determined from the point where the derivative signal crosses the baseline if the lines are either asymmetric or overlapped.

The field positions are listed in Table V (as proton frequencies) and were normalized to the same, arbitrary, microwave frequency. The widths of the lines in both spectra were about $\delta = 20$ mG. The consistency of the results, as shown by the data in Table VI, which gives differences in line positions, is of the order of 2–3 cps in proton frequency, i.e., ~ 2 parts in 10^7, or ~ 0.5 mG.

Since the second-order shifts were not resolved, the usual theory[21,25] indicates that all the lines of N^- should be shifted by the same amount, and the spectrum centers calculated from the mean positions

$$(\tfrac{1}{2})[B(M_\alpha, M_\beta) + B(-M_\alpha, -M_\beta)],$$

of all pairs of corresponding lines on the high- and low-field sides of the spectrum should be the same. Centers calculated in this way are given in the last column of Table V, and except for the center of the $[\tilde{M}_\alpha, \tilde{M}_\beta] = [\bar{2},0], [2,0]$ pair for N^-, the maximum spread within each radical is 1 part in 7×10^6. This level of consistency is the same as exhibited by the line-position differences in Table VI and thus the 16-cps (4-mG) discrepancy from the $[\bar{2},0], [2,0]$ pair is well outside the experimental errors. Corrections higher than second order cannot be large enough to cause this disagreement, and we have consequently examined the validity of the assumption that the linewidths are large enough compared to the second-order shifts to permit an averaging over the different components within a degenerate line.

The spectrum was calculated numerically for the

$[\pm 2,0], [\pm 1,0]$, and $[\pm 1, \pm 1]$ lines using an IBM-7094 computer with a spectrum-simulation program developed by Goodman[59] and Kaplan.[29] The results of the calculation are presented in Table VII, where the shifts are given for a range of widths from $\delta = 0$ to 100 mG using Eq. (A1) for the positions of the individual components. The line shapes were assumed to be Lorentzian and each component was taken to be of the same width (δ). The shift data in the table for each width is the position halfway between the extrema of the first derivative of each line. Apparent widths were not readily obtained from the computer program as set up for this particular problem.

The results in Table VII show that for linewidths less than 30 mG the lines are not equally shifted, and only for the $[\pm 2,0]$ lines are the shifts equal to the value expected from a weighted average of all the degenerate components. The $[\pm 1,0]$ and $[\pm 1, \pm 1]$ lines have apparent shifts that first *increase* and then decrease as the lines narrow, and they split up into two partially resolved components for widths less than 15 mG. One of these two components is shifted by about 5 mG and is strong, while the other is weaker and is shifted by about 20 mG. The $[0,0]$ line splits into two components for $\delta = 10$ and 15 mG, and into three for $\delta = 5$ mG. Since the apparent shift, and undoubtedly the shape, of the degenerate lines changes rapidly for widths below about 20–25 mG, a detailed study of these effects might make it possible to obtain a quite precise indirect estimate of the true linewidth, provided, of course, that microwave power saturation is unimportant and no distortions are introduced by the spectrometer.

The calculations given in Table VII show that for linewidths of about 15 mG the $[\pm 1,0]$ and $[\pm 1, \pm 1]$ lines would appear in an experimental spectrum as a single line with a shift of about 5 mG, or 3.5 mG smaller in magnitude than the shift of the $[\pm 2,0]$ lines. These calculations are thus entirely consistent with the experimental data (Table V) since the spectrum centers calculated from the $[\pm 1,0]$ and $[\pm 1, \pm 1]$ lines are at fields 4 mG higher than the center calculated from the $[\pm 2,0]$ lines.

To compare the g values of the N^- and N^--d_8 radicals, calculations of the second-order shift must also be made for N^--d_8. Since the shift is $\sim a^2/B_0$, the departures from averaging found for the proton lines will not be of significance for the deuteron lines, and the shift can be computed directly from Eq. (A1). The allowed values of J_α are $J_\alpha = 0, 1, 2, 3$, and 4 with degeneracies $D_{J_\alpha} = 3, 6, 6, 3$, and 1, respectively, and similarly for J_β. The shifts of the different lines are no longer, in general, identical when the spin I is not equal to $\tfrac{1}{2}$, but direct calculation from Eq. (A1) gives the same shift within about 0.005 mG for the $[\pm 1,0], [0, \pm 1]$, and $[\pm 1, \pm 1]$ lines of N^--d_8. Its value is 2.4 cps (proton

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[59] S. Goodman, thesis, Columbia University, New York, 1962.

frequency) or 0.56 mG. If the g values of N^- and $N^- \text{-} d_8$ were the same, the center of the N^- spectrum calculated from the $[\pm 2,0]$ lines would be $8.5-0.6=7.9$ mG lower in field than the center of the $N^- \text{-} d_8$ spectrum. The experimentally observed difference between the centers calculated from the $[\pm 2,0]$ lines of $N^- (13962.025$ kc/sec) and from the $N^- \text{-} d_8$ lines $(13962.050$ kc/sec) is 25 cps or 5.9 mG, so that the true center of the $N^- \text{-} d_8$ spectrum is $7.9-5.9=2.0$ mG lower than the true center of the N^- spectrum. This difference is about four times the error in determining the centers (as estimated from the reproducibility of the data in Table V), and indicates that the g value of $N^- \text{-} d_8$ is greater than that of N^- by about 0.7 ppm, or $g(N^- \text{-} d_8) = g(N^-) + (0.0000014 \pm 0.0000003)$. The best absolute measurement of the g value[26] of N^- is $g(N^-) = 2.002752 \pm 0.000006$.

Results such as these, in which differences in positions of the order of 10% of the linewidths are observed, must, of course, be interpreted with caution. A small but consistent asymmetry in the line shapes of one of the radicals which was different from a consistent asymmetry in the line shapes of the other radical could produce a systematic error. The degree of asymmetry was examined, and in none of the lines studied did the positive and negative deflections in the first-derivative spectrum of a line differ appreciably. Although small instrumental factors might mask a difference in asymmetry, both radicals were in the same solution, and thus these differences should all be quite small.

Resonant States of H_2^-*

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(Received 6 December 1966)

Detailed quantitative calculations are reported for different resonant states of H_2^-. Results tie in quantitatively with dissociative attachment experiments and electron-scattering experiments, and qualitatively with vibrational-excitation experiments. Preliminary results on other states which have not as yet been experimentally observed are also discussed. Wavefunctions and energies are reported.

INTRODUCTION

In this paper the quasivariation method developed simultaneously by Taylor and Williams[1] (hereinafter denoted by TW) and O'Malley and Geltman[2] and the stabilization method discussed in the work of Taylor, Nazaroff, and Golebiewski[3] (hereinafter denoted by TNG) are applied to the *ab initio* calculation of quasistationary states of H_2^-. Results are compared quantitatively and qualitatively to dissociative attachment, vibrational-excitation and electron-scattering experiments.

For the definitions of, and distinctions between the three types of resonance calculated here (single particle and core-excited Types I and II, hereinafter denoted by SP, CE1, and CE2, respectively), the usefulness of these definitions and a discussion and derivation of the variational principles used in the present work, see the paper of TNG.[3]

RESULTS AND DISCUSSION

The calculations presented here are closely connected with experiments in which resonances are seen in the total and inelastic electron–hydrogen cross section.[4-8] These resonances are attributed to the formation of two short-lived states of H_2^-, and the individual peaks in the cross section correspond to definite vibrational levels of the resonant molecular state. The well-developed vibrational structure indicates a lifetime

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