

CHAPTER 3 - THE MAGNETIC ANISOTROPIES OF THE METHYL HALIDES

3.1 INTRODUCTION

The magnetic anisotropies of the methyl halides have been the subject of various investigations by different techniques, in particular, the molecular Zeeman effect in beam-maser or microwave spectroscopy which has been the most prolific source of reliable magnetic anisotropies, the Cotton-Mouton effect, and the most recent method developed, high-field NMR spectroscopy, first exploited by Lohman and MacLean.¹

From applications of the microwave Zeeman effect, the magnetic anisotropies of CH_3Cl , CH_3Br , CH_3I ² and CH_3F ³ were derived in 1970 and 1974, and that of CH_3Cl was much more precisely specified in 1978 by the beam-maser Zeeman method.⁴ In 1988, a value for the magnetic anisotropy for CH_3Cl was obtained from measurements of the temperature dependence of the vapour-phase Cotton-Mouton effect⁵ and, also in 1988, the magnetic anisotropies of CH_3F , CH_3Br and CH_3I were deduced from the ^2H NMR spectra of the deuterated compounds.⁶ In view of the conclusion in the report of the NMR investigation that the magnetic anisotropy of CH_3I as determined by the microwave Zeeman method is about 14% too high, measurements of the Cotton-Mouton effects of CH_3F , CH_3Br and CH_3I were conducted so as to establish a basis for comparison of results from the three methods. This study⁷ complements an earlier investigation of CH_4 and CH_3Cl carried out by Lukins and Ritchie.⁵

In order to obtain reliable values for the magnetic anisotropies, it was necessary to undertake temperature dependence studies of the effect so as to separate the orientation and distortion contributions, and this provided useful information about the magnetic hyperpolarizability anisotropy, another molecular property that is of interest.

3.2 EXPERIMENTAL RESULTS

Samples used were as follows: methyl fluoride (Matheson, >99.0%) and methyl bromide (Fluka, >99%), used without further treatment; methyl iodide (Fluka, >99%), washed successively with dilute sodium thiosulfate, water, dilute sodium carbonate and water, then dried with calcium chloride, distilled from phosphorus pentoxide, and stored with silver wool.⁸ The compounds were analyzed by gas chromatography and the purity of each compound was confirmed to be $\geq 99.5\%$; errors arising from impurities were therefore considered to be negligible. In addition, methyl iodide, a liquid, was subjected to several freeze-pump-thaw-distil cycles in the vapour-handling system immediately prior to the commencement of pressure dependence measurements.

In the case of methyl fluoride, the smallness of the Cotton-Mouton effect and of the available gas sample precluded a temperature dependence study, and the measurements were confined to duplicate runs, over pressure ranges up to 980 kPa, at two temperatures (296.2, 296.1 K) in the vicinity of room temperature. For methyl bromide and methyl iodide, measurements were performed over ranges of pressure and temperature (CH₃Br, 10 temperatures, 294-422 K, maximum pressure 229 kPa; CH₃I, 12 temperatures, 295-467 K, maximum pressure 119 kPa).

Gas densities were calculated from measured gas pressures and temperatures using published density second (and, in the case of methyl fluoride, third) virial coefficients.⁹ Cotton-Mouton second virial coefficients were not detectable under the conditions of these experiments. Results of measurements on these compounds are summarized in Tables 3.1, 3.2 and 3.3, where the uncertainties shown are based on the standard deviations derived from least-squares straight lines.

Except for a preliminary investigation of methyl fluoride, made almost 25 years ago with a less sensitive version of the present equipment,¹⁰ the vapour-phase Cotton-Mouton constants of these three molecules have not previously been determined; a value of the solution-phase Cotton-Mouton constant of methyl iodide in carbon tetrachloride at 298 K has been reported.¹¹

3.3 ANALYSIS AND DISCUSSION

For molecules with an axis of three-fold or higher symmetry, the expression for the temperature dependence of the Cotton-Mouton constant is described by the equation:

$${}_mC = \frac{N_A \mu_0^2}{270 \epsilon_0} \left(\Delta\eta + \frac{2\Delta\alpha\Delta\chi}{3kT} \right) \quad (3.1)$$

in which $\Delta\eta \left(= \eta_{\alpha\beta:\alpha\beta} - \frac{1}{3} \eta_{\alpha\alpha:\beta\beta} \right)$, $\Delta\alpha (= \alpha_{zz} - \alpha_{xx})$ and $\Delta\chi (= \chi_{zz} - \chi_{xx})$ are the anisotropies in the magnetic hyperpolarizability, the optical-frequency electric polarizability, and the magnetizability, respectively. The linear dependence on T^{-1} predicted by the above equation was observed for methyl bromide and methyl iodide and is shown in Figure 3.1 from which, following extrapolation to $T^{-1} = 0$, the intercept determines $\Delta\eta$ and the slope $\Delta\chi$, provided that $\Delta\alpha$ is independently known.

TABLE 3.1 COTTON-MOUTON EFFECT OF METHYL FLUORIDE AT $\lambda = 632.8$ nm

T / K	No. of pressures	Maximum p / kPa	$10^6 B / \text{m}^3 \text{mol}^{-1}$ (a)	$10^{12} C / \text{m}^6 \text{mol}^{-2}$ (b)	$10^{27} {}_m C / \text{m}^5 \text{A}^{-2} \text{mol}^{-1}$
296.2	7	980	-209	21 790	-0.195 ± 0.007
296.1	9	930	-209	21 790	-0.198 ± 0.006

(a) Density second virial coefficients taken from reference 9.

(b) Density third virial coefficients taken from reference 9.

TABLE 3.2 COTTON-MOUTON EFFECT OF METHYL BROMIDE AT $\lambda = 632.8$ nm

T / K	No. of pressures	Maximum p / kPa	$10^6 B / \text{m}^3 \text{mol}^{-1}$	$10^{27} {}_m C / \text{m}^5 \text{A}^{-2} \text{mol}^{-1}$
421.7	10	229	-250	-1.30 ± 0.08
410.2	9	178	-260	-1.34 ± 0.04
402.6	9	211	-278	-1.34 ± 0.05
389.1	9	227	-283	-1.40 ± 0.05
378.1	10	188	-296	-1.51 ± 0.04
351.4	9	208	-346	-1.58 ± 0.03
334.1	6	171	-390	-1.72 ± 0.05
317.4	10	203	-448	-1.80 ± 0.02
304.8	9	169	-502	-1.87 ± 0.04
294.2	9	168	-560	-1.96 ± 0.05

TABLE 3.3 COTTON-MOUTON EFFECT OF METHYL IODIDE AT $\lambda = 632.8$ nm

T / K	No. of pressures	Maximum p / kPa	$10^6 B / \text{m}^3 \text{mol}^{-1}$	$10^{27} {}_m C / \text{m}^5 \text{A}^{-2} \text{mol}^{-1}$
466.8	10	90	-360	-1.81 ± 0.08
448.6	6	119	-370	-2.00 ± 0.10
442.8	11	118	-370	-1.92 ± 0.07
407.9	5	111	-380	-1.97 ± 0.07
405.8	5	35	-380	-2.07 ± 0.13
390.2	9	35	-400	-2.35 ± 0.10
358.3	9	95	-470	-2.51 ± 0.06
334.6	9	95	-560	-2.55 ± 0.05
315.5	11	30	-700	-2.90 ± 0.08
311.1	8	41	-700	-2.81 ± 0.06
297.2	9	37	-800	-3.08 ± 0.10
295.3	7	30	-800	-3.13 ± 0.10

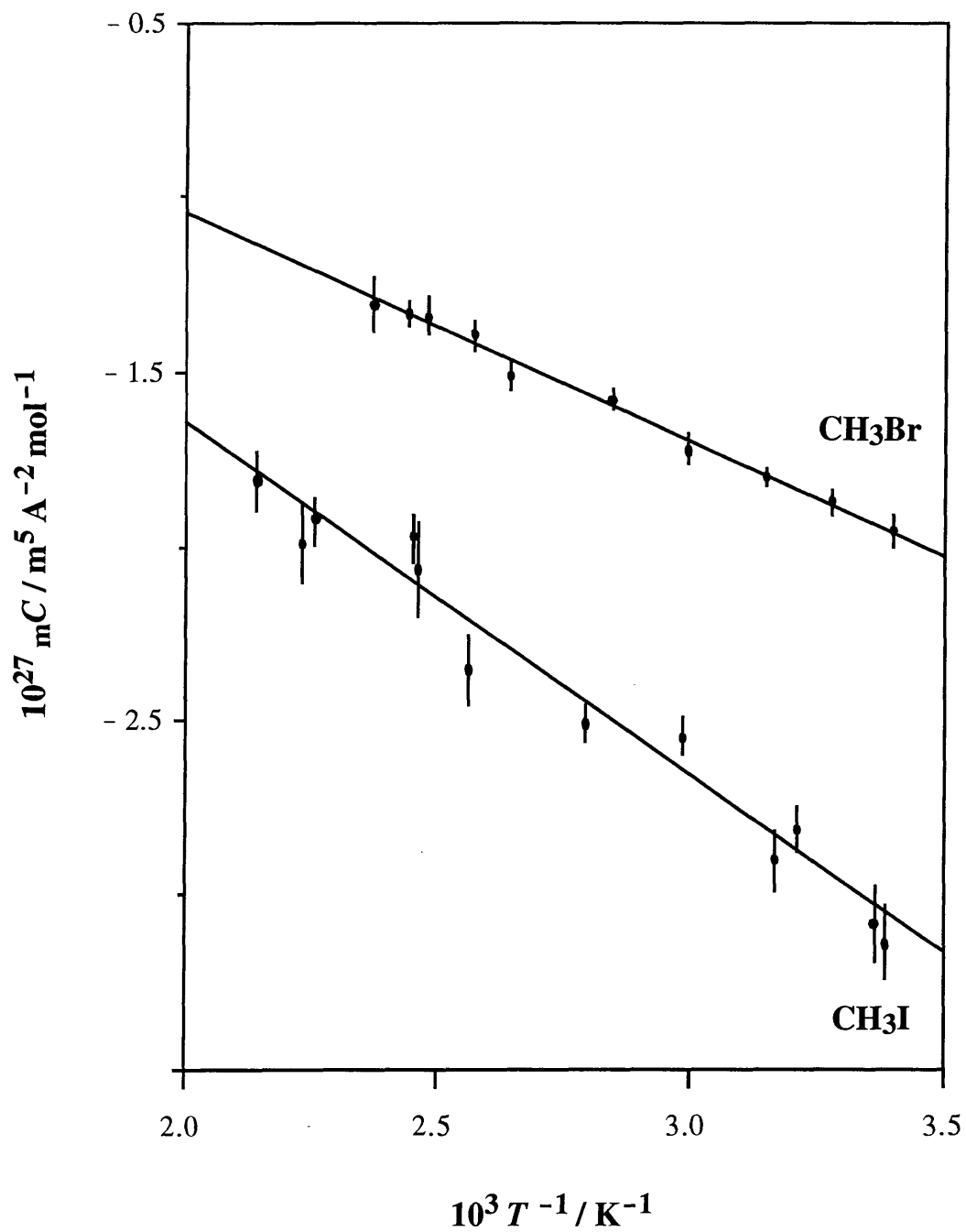


Figure 3.1 Temperature dependence of the vapour-state Cotton-Mouton constants of CH₃Br and CH₃I.

When fitting values of ${}_mC$ to a linear equation in T^{-1} , using a least-squares program written by Gentle,¹² the data points were weighted according to the statistical uncertainty involved in determining the slope of φ against ρ . Table 3.4 contains a complete analysis of the Cotton-Mouton effects of these three molecules, and for comparison methyl chloride, in terms of the magnetic hyperpolarizability anisotropy, the magnetic anisotropy, and the individual components of the magnetizability.

In the case of CH_3F , the estimate of $\Delta\eta$ was derived from the single-temperature data in Table 3.1, together with the known values of $\Delta\alpha$ and $\Delta\chi$ for this molecule; for CH_3Cl , CH_3Br and CH_3I , this quantity was obtained directly from the $T^{-1} = 0$ intercept of the appropriate weighted-fit least-squares straight line. Because of the long extrapolations that are required or, for CH_3F , other uncertainties, the values of $\Delta\eta$ that emerge, the first for these molecules, are of rather low precision. For all four, the proportions of the relatively small Cotton-Mouton constants at 298 K that originate in the temperature-independent contributions are minor (CH_3F , $\approx -5\%$; CH_3Cl , CH_3Br , CH_3I , $\approx -13\%$), and further improvement of the apparatus would be necessary for any significant improvement in the precision of the intercepts. Despite the small contribution by the temperature-independent term, failure to take account of $\Delta\eta$ would lead to values of $\Delta\chi$ whose magnitudes would be underestimated by $\approx 10\%$.

As expected from the earlier results for CH_4 and CH_3Cl ,⁵ $\Delta\eta$ is found to be positive in sign for CH_3F , CH_3Br and CH_3I , and, despite the large uncertainties, to increase in magnitude across the complete series as the size of the substituent increases. Since the magnetic hyperpolarizability tensor describes the quadratic response of the electric polarizability tensor to a magnetic induction,^{13,14} $\Delta\eta$ might reasonably be predicted, at least in molecules of the same symmetry, to be proportional to the mean polarizability, α , which can be related to the molecular size. The relevant data^{5,15,16} (substituent, $10^{40} \alpha / \text{C m}^2 \text{V}^{-1}$, $10^{50} \Delta\eta / \text{C m}^2 \text{V}^{-1} \text{T}^{-2}$) for

TABLE 3.4 ANALYSIS OF THE COTTON-MOUTON EFFECTS OF THE METHYL HALIDES

Property	Value			
	CH ₃ F	CH ₃ Cl	CH ₃ Br	CH ₃ I
10^{27} intercept / $\text{m}^5 \text{A}^{-2} \text{mol}^{-1}$	-	0.19 ± 0.13	0.26 ± 0.06	0.39 ± 0.19
10^{24} slope / $\text{m}^5 \text{A}^{-2} \text{K mol}^{-1}$	-	-0.492 ± 0.039	-0.654 ± 0.021	-1.018 ± 0.066
$10^{50} \Delta\eta$ / $\text{C m}^2 \text{V}^{-1} \text{T}^{-2}$	2 ± 13	47 ± 33	66 ± 15	99 ± 47
$10^{40} \Delta\alpha$ / $\text{C m}^2 \text{V}^{-1}$ (a)	0.225 ± 0.033	1.705 ± 0.054	2.253 ± 0.045	2.946 ± 0.059
$10^{29} \Delta\chi$ / J T^{-2}	-14.1 ± 1.0 (b)	-15.0 ± 1.3	-15.1 ± 0.8	-18.0 ± 1.5
$10^{29} \chi$ / J T^{-2} (c)	-29.6	-53.1	-71.1	-95.0
$10^{29} \chi_{zz}$ / J T^{-2}	-39.0	-63.1	-81.2	-107.0
$10^{29} \chi_{xx}$ / J T^{-2}	-24.9	-48.1	-66.1	-89.0

(a) Optical-frequency ($\lambda = 632.8$ nm) polarizability anisotropies from references 15 and 16.

(b) Reference 3.

(c) Mean molecular magnetizabilities, $\chi = \frac{1}{3}(\chi_{zz} + 2\chi_{xx})$, from reference 30.

the molecules of interest (H, 2.89, 11.3 ± 1.5 ; F, 2.90, 2 ± 13 ; Cl, 5.04, 47 ± 33 ; Br, 6.22, 66 ± 15 ; I, 8.41, 99 ± 47) are displayed in Figure 3.2, and appear to support a relationship of this kind. It should be noted that the experimental value of $\Delta\eta$ for methane is far more precisely determined than those for the halogenomethanes, because the normally dominant orientation contribution to the Cotton-Mouton constant is absent, and the effect arises entirely from the magnetic hyperpolarizability anisotropy. Values of $\Delta\eta$ are available for a range of small molecules, but few, if any, trends have previously been identified. Experimental (that is, Cotton-Mouton effect) and *ab initio* values of $\Delta\eta$ are available and summarized in Table 3.5 for the rare gases He, Ne, Ar, Kr and Xe, and a plot, shown in Figure 3.3, of $\Delta\eta$ against the mean polarizability values²⁵ indicates some further support for a correlation of the kind noted above. Clearly, there is no firm basis to suggest that $\Delta\eta$ can be estimated solely from α , but these investigations indicate scope for further work in this area.

In order to deduce the magnetic anisotropies, $\Delta\chi$, from the slopes of the plots of ${}_mC$ against T^{-1} (or, in the case of CH_3F , to determine $\Delta\eta$), reliable optical-frequency polarizability anisotropies, $\Delta\alpha$, at $\lambda = 632.8$ nm, usually obtained from vapour-phase Rayleigh depolarization ratios and refractivities,¹⁵ are required. However, for CH_3F , a very weakly anisotropic molecule, it was recognized¹⁶ that the depolarization ratio, and therefore the value of $\Delta\alpha$, obtained by the conventional method^{15,26} are overestimates, because of the inclusion of a spurious and significant contribution from the depolarized vibrational Raman spectrum. Fortunately, CH_3F has been examined by the electrooptical Kerr effect²⁷ and the Raman spectroscopic method,²⁸ both of which circumvent this difficulty, thus a reliable experimental value of $\Delta\alpha$, subsequently confirmed by *ab initio* molecular-orbital calculations,²⁹ was available for this analysis. By contrast, CH_3Cl , CH_3Br and CH_3I are much more anisotropic, and the depolarization ratios¹⁵ for these molecules are sufficiently large

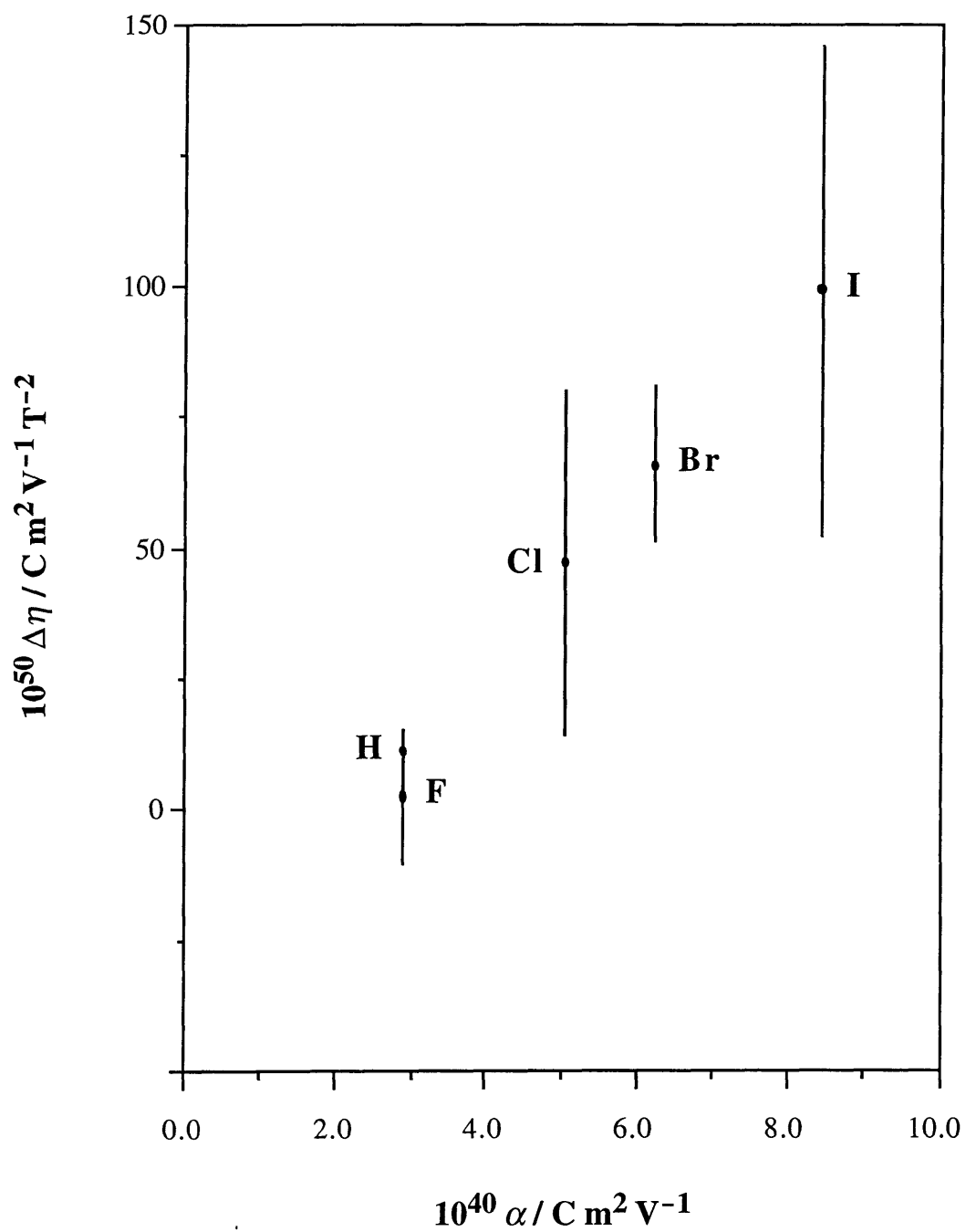


Figure 3.2 Variation of the magnetic hyperpolarizability anisotropy with the mean polarizability in the series CH_3X ($\text{X} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{I}$).

TABLE 3.5 VALUES OF MAGNETIC HYPERPOLARIZABILITY ANISOTROPIES, $\Delta\eta$,^(a) FOR THE RARE GASES

	Theory ^(b)	Experiment
He	0.143 ^(c)	0.12 ± 0.02 ($\lambda = 514.5$ nm) ^(g)
	0.142 ^(d)	0.16 ± 0.16 ($\lambda = 632.8$ nm) ^(h)
	0.158 ^(e)	
	0.142 (SCF), 0.154 (MP2) ^(f)	
Ne	0.398 ± 0.02 (MC SCF) ⁽ⁱ⁾	0.187 ± 0.010 ($\lambda = 514.5$ nm) ^(j)
	0.460 ^(e)	0.61 ± 0.45 ($\lambda = 632.8$ nm) ^(h)
	0.329 (SCF), 0.452 (MP2) ^(f)	
Ar	4.04 ^(e)	4.2 ± 1.4 ($\lambda = 514.5$ nm) ^(k)
	3.32 (SCF), 3.82 (MP2) ^(f)	3.88 ± 0.22 ($\lambda = 632.8$ nm) ^(h)
Kr	8.56 ^(e)	6.73 ± 0.44 ($\lambda = 632.8$ nm) ^(h)
Xe	20.6 ^(e)	15.9 ± 0.8 ($\lambda = 632.8$ nm) ^(h)

(a) Expressed as $10^{50} \Delta\eta / \text{C m}^2 \text{V}^{-1} \text{T}^{-2}$.

(b) Static values quoted unless otherwise shown.

(c) Reference 14. (d) Reference 17. (e) Reference 18.

(f) Reference 19. (g) Reference 20. (h) Reference 21.

(i) At $\lambda = 632.8$ nm, reference 22. (j) Reference 23. (k) Reference 24.

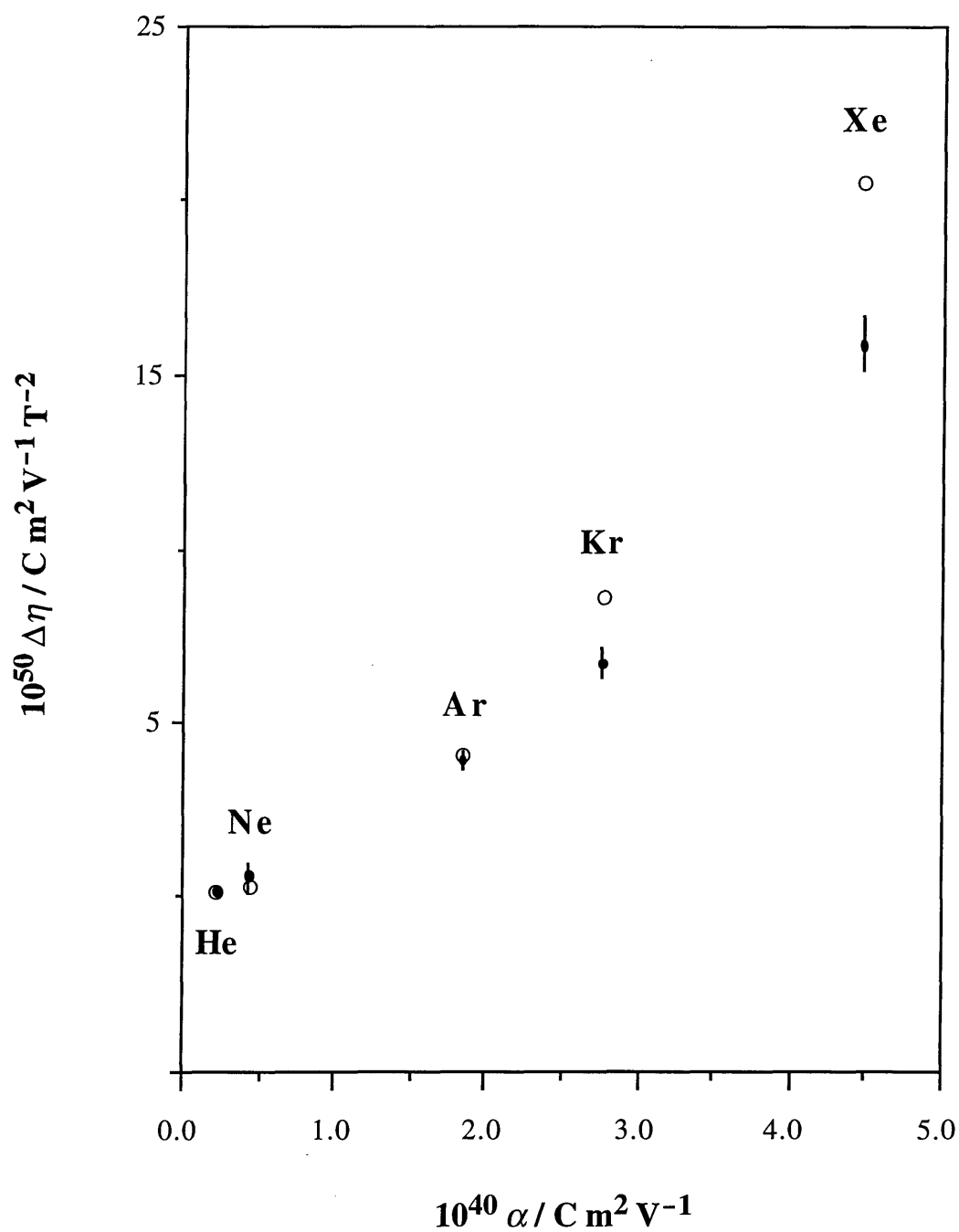


Figure 3.3 Variation of the magnetic hyperpolarizability anisotropy with the mean polarizability for the rare gases (He, Ne, Ar, Kr, Xe).

Open circles are values taken from reference 18; experimental points from reference 21. Theoretical and experimental values overlap for He, Ne and Ar.

not to be affected by inclusion or exclusion of the vibrational Raman spectrum. The values of $\Delta\chi$ derived from the Cotton-Mouton effects of CH_3Cl , CH_3Br and CH_3I , and also the previously reported microwave Zeeman spectroscopic result for CH_3F , are shown in Table 3.6. Combination of these with the known mean magnetizabilities³⁰ yields the individual components, χ_{zz} and χ_{xx} , of the magnetizability. Obviously, the direction of maximum (negative) magnetizability is parallel rather than perpendicular to the C - X axis; and, since $|\Delta\chi|$ increases only slightly through the series, replacement of F by the larger halogens Cl, Br and I augments χ_{zz} and χ_{xx} to about the same extent.

It is of interest to compare the present values of $\Delta\chi$ for CH_3Cl , CH_3Br and CH_3I , derived from measurements of the Cotton-Mouton effects of these species in the vapour state, with those previously obtained from observations of the molecular Zeeman effect^{2,4} and others from a method that exploits the electric quadrupole splittings that appear in the high-field ^2H NMR spectra of deuterated methyl halides in the dilute-solution state.⁶ From the summary in Table 3.6, it can be seen that the results from the Cotton-Mouton effect and the molecular Zeeman effect are in good agreement, insofar as in each case the difference between the values is less than the sum of the uncertainties. The report of the NMR spectroscopic study does not explicitly state the likely errors, although an earlier investigation³¹ by the same authors estimated these as 3-7%. However, for all three molecules, the results obtained by the NMR method appear to be consistently lower than those from both the Cotton-Mouton and Zeeman methods, especially the former. In view of the concordance between the Cotton-Mouton and Zeeman values for CH_3I , the suggestion⁶ that the latter result for this molecule is perhaps 14% too high cannot be supported.

Finally, it is relevant to consider some important features of the three methods

TABLE 3.6 COMPARISON OF EXPERIMENTAL VALUES OF THE
MAGNETIC ANISOTROPIES ^(a) OF THE METHYL HALIDES

Method	Value			
	CH ₃ F	CH ₃ Cl	CH ₃ Br	CH ₃ I
Cotton-Mouton effect, vapour state	-	-15.0 ± 1.3 ^(b)	-15.1 ± 0.8 ^(c)	-18.0 ± 1.5 ^(c)
Microwave Zeeman effect, vapour state	-14.1 ± 1.0 ^(d)	-13.2 ± 0.7 ^(e) -13.90 ± 0.03 ^(f)	-14.1 ± 0.7 ^(e)	-18.2 ± 0.8 ^(e)
95.2 MHz ² H NMR spectra, dilute-solution state ^(g)	-	-12.5	-12.5	-15.9

^(a) Expressed as $10^{29} \Delta\chi / \text{J T}^{-2}$. ^(b) Reference 5. ^(c) Present work. ^(d) Reference 3.

^(e) Reference 2. ^(f) Reference 4. ^(g) Reference 6.

that have been used to obtain the magnetic anisotropies of the diamagnetic molecules of interest here. The Cotton-Mouton effect is applicable to dipolar and non-dipolar species, and is unaffected by the presence or absence of quadrupolar nuclei; the microwave Zeeman effect requires that the molecule possess a permanent electric dipole moment, even if only a small moment introduced by judicious isotopic substitution; and the NMR method exploits the small quadrupolar splitting that appears, as a consequence of molecular orientation at high fields (14.6 T), in the ^2H NMR spectra of monodeuterated compounds. As can be seen from the data in Tables 3.1, 3.2 and 3.3, which are typical of weakly anisotropic aliphatic compounds, it is necessary to perform the measurements of the Cotton-Mouton effect over a wide range of pressure (so as to increase the magnitude of the effect) and temperature (so as to separate the temperature-independent and temperature-dependent contributions to the effect). The microwave spectroscopic observations are made at very low pressures (≈ 1 Pa), an obvious advantage for involatile or reactive species; and the NMR spectra are obtained from dilute solutions (≈ 5 -10 mol %) of the deuterated solute in solvents such as cyclohexane or diethyl ether. Measurements of the Cotton-Mouton effect are usually straightforward, and the only additional parameter needed to evaluate the magnetic anisotropy is the optical-frequency polarizability anisotropy, normally measurable to high precision. The analysis of the microwave Zeeman spectra of molecules that contain heavier halogen atoms (Cl, Br and I) is complicated by nuclear quadrupolar interactions, while difficulties in the interpretation of the quadrupolar splitting in the NMR spectra appear to arise in relation to the value of the quadrupolar coupling constant to be used and the effect of the solvent on the apparent molecular properties. For these reasons, the three methods to which reference is made here should be considered as complementary, and the present study has highlighted the usefulness of such comparisons.

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CHAPTER 4 - THE MAGNETIC ANISOTROPY AND THE QUADRUPOLE MOMENT OF ACETYLENE

4.1 INTRODUCTION

Over the past thirty years, the magnetic anisotropy and, in particular, the quadrupole moment of acetylene have attracted considerable interest, and a wide range of experimental and theoretical methods has been used in attempts to determine the numerical values of these important molecular properties. Measurements of the temperature dependence of the Cotton-Mouton effect conducted by Kling, *et al.*,¹ were used to obtain the first direct experimental value of the magnetic anisotropy of acetylene, and the combination of this result with the known rotational g value² provided a value of the quadrupole moment of this molecule that agreed with state-of-the-art SCF calculations.³ Since then, however, other experimental techniques⁴ and considerably improved theoretical procedures⁵ have been exploited, and it is now clear that the true values of the quadrupole moment and, as a consequence, the magnetic anisotropy are significantly smaller in magnitude than had previously been reported. In view of the importance of these fundamental properties, and because of the doubt that has arisen in relation to the earlier measurements, it was considered worthwhile to re-investigate the Cotton-Mouton effect of acetylene.⁶

4.2 EXPERIMENTAL RESULTS

Acetylene (C.I.G. instrument grade, 99.5%, dissolved in acetone) was passed through two traps in an ice-water-salt mixture to condense acetone vapour and, immediately before each series of measurements, subjected to two freeze-pump-thaw

cycles in the vapour-handling system. Gas-chromatographic analyses indicated sample purities of at least 99.8%. Errors arising from impurities were considered negligible; any traces of acetone that may have been present were regarded as insignificant since acetone is very weakly anisotropic. The magnetic field-induced birefringence at $\lambda = 632.8$ nm was measured at 21 temperatures in the range 293-442 K and, at each temperature, at several pressures not exceeding ≈ 200 kPa, due to safety reasons.

Gas densities were calculated from measured gas pressures and temperatures using published density second virial coefficients.⁷ The results of measurements are summarized in Table 4.1, where the uncertainties shown are based on the standard deviations derived from least-squares straight lines.

It is of interest to compare the present results with those of the earlier Cotton-Mouton effect study,¹ which was performed at ≈ 37 temperatures in the range ≈ 199 -391 K, a span of 192 K rather than 149 K, and, similarly, at pressures up to ≈ 100 kPa, and these are discussed in the next section.

4.3 ANALYSIS AND DISCUSSION

For molecules with an axis of three-fold or higher symmetry, the equation describing the temperature dependence of ${}_mC$ is:

$${}_mC = \frac{N_A \mu_0^2}{270 \epsilon_0} \left(\Delta\eta + \frac{2\Delta\alpha\Delta\chi}{3kT} \right) \quad (4.1)$$

in which the terms have the usual meanings. This equation predicts a linear dependence of ${}_mC$ on T^{-1} , which was indeed observed, and this is shown in Figure

TABLE 4.1 COTTON-MOUTON EFFECT OF ACETYLENE AT $\lambda = 632.8$ nm

T / K	No. of pressures	Maximum p / kPa	$10^6 B / \text{m}^3 \text{mol}^{-1}$	$10^{27} {}_m C / \text{m}^5 \text{A}^{-2} \text{mol}^{-1}$
442.2	7	100.5	-41.5	-0.339 ± 0.026
417.8	8	98.0	-49.3	-0.390 ± 0.017
415.6	6	96.7	-49.7	-0.392 ± 0.024
414.6	8	101.8	-50.4	-0.396 ± 0.024
399.5	6	97.9	-54.0	-0.394 ± 0.010
396.4	10	101.7	-58.1	-0.362 ± 0.018
396.0	5	101.7	-58.1	-0.379 ± 0.050
378.1	9	101.8	-67.7	-0.398 ± 0.026
377.6	7	101.9	-84.1	-0.380 ± 0.016
360.8	6	91.5	-93.6	-0.422 ± 0.017
346.0	9	99.6	-103.6	-0.433 ± 0.021
330.4	7	92.7	-107.3	-0.436 ± 0.022

Table 4.1 continues on next page

329.9	7	93.2	-116.4	-0.460 ± 0.016
318.7	7	99.6	-122.1	-0.483 ± 0.020
310.1	9	101.7	-136.4	-0.498 ± 0.014
305.8	7	97.1	-141.4	-0.492 ± 0.025
298.7	8	99.5	-145.1	-0.514 ± 0.017
297.2	9	95.2	-152.4	-0.506 ± 0.010
295.1	7	98.0	-155.3	-0.561 ± 0.018
293.5	7	92.5	-157.5	-0.535 ± 0.027
293.1	10	101.6	-166.4	-0.556 ± 0.023

4.1. If the line is extrapolated to $T^{-1} = 0$, the intercept determines $\Delta\eta$ and the slope $\Delta\chi$, provided that $\Delta\alpha$ is independently known. The results of a weighted least-squares fitting procedure and subsequent analysis in terms of the relevant molecular properties are summarized in Table 4.2, where results from the previous study¹ are shown for comparison.

Further comparison is detailed in Figure 4.2: line A (present measurements) is the weighted-fit least-squares straight line derived from the results in Table 4.1 (with the actual points shown); line B is the line defined by the slope and intercept reported in the previous study (without the actual data points shown). Over the temperature range (293-391 K) that is common to the two investigations, the absolute values of the small Cotton-Mouton constant of acetylene differ by less than 10%; however, the actual data sets and the long extrapolations to $T^{-1} = 0$ produce seriously discordant values of the intercepts and slopes and, as shown in Table 4.2, the derived molecular properties.

It is immediately obvious that the value of $\Delta\eta$ (expressed as $10^{50}\Delta\eta / \text{C m}^2\text{V}^{-1}\text{T}^{-2}$) and the percentage contribution that it makes to the Cotton-Mouton constant at 298 K (3 ± 8 , $-2 \pm 6\%$) are very much smaller than indicated by the earlier measurements (68 ± 5 , $-48 \pm 4\%$). Nevertheless, there are no immediately obvious qualitative grounds for a choice between these results, as such values are often poorly determined by experiments of this kind and, unfortunately, *ab initio* computations of this property have not yet been extended to species of this complexity.

Using the optical-frequency polarizability anisotropy at $\lambda = 632.8 \text{ nm}$,⁸ the magnetic anisotropy was derived from equation (4.1), and, with the mean magnetizability,⁹ the individual components of the magnetizability were evaluated.

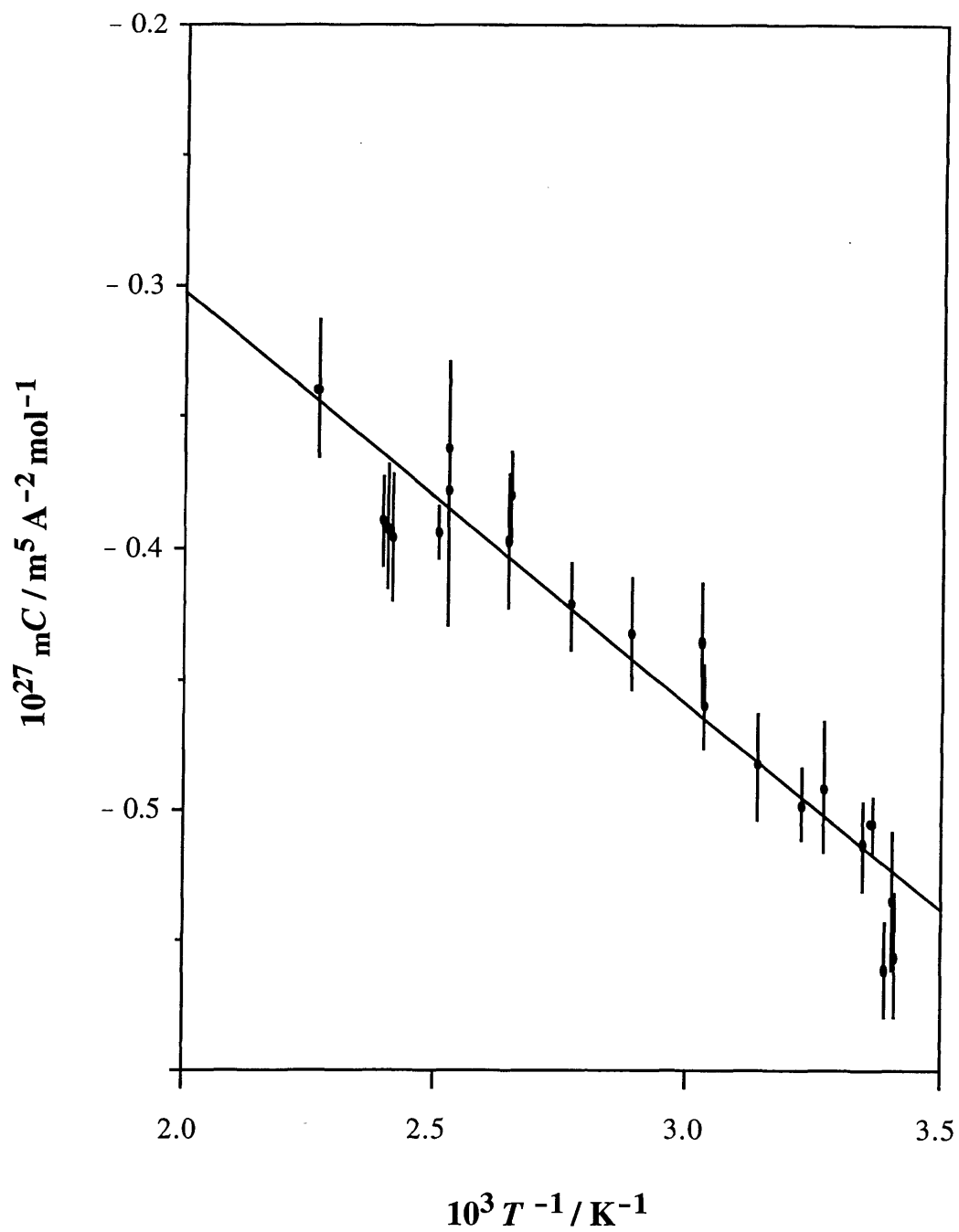


Figure 4.1 Temperature dependence of the Cotton-Mouton constant of acetylene.

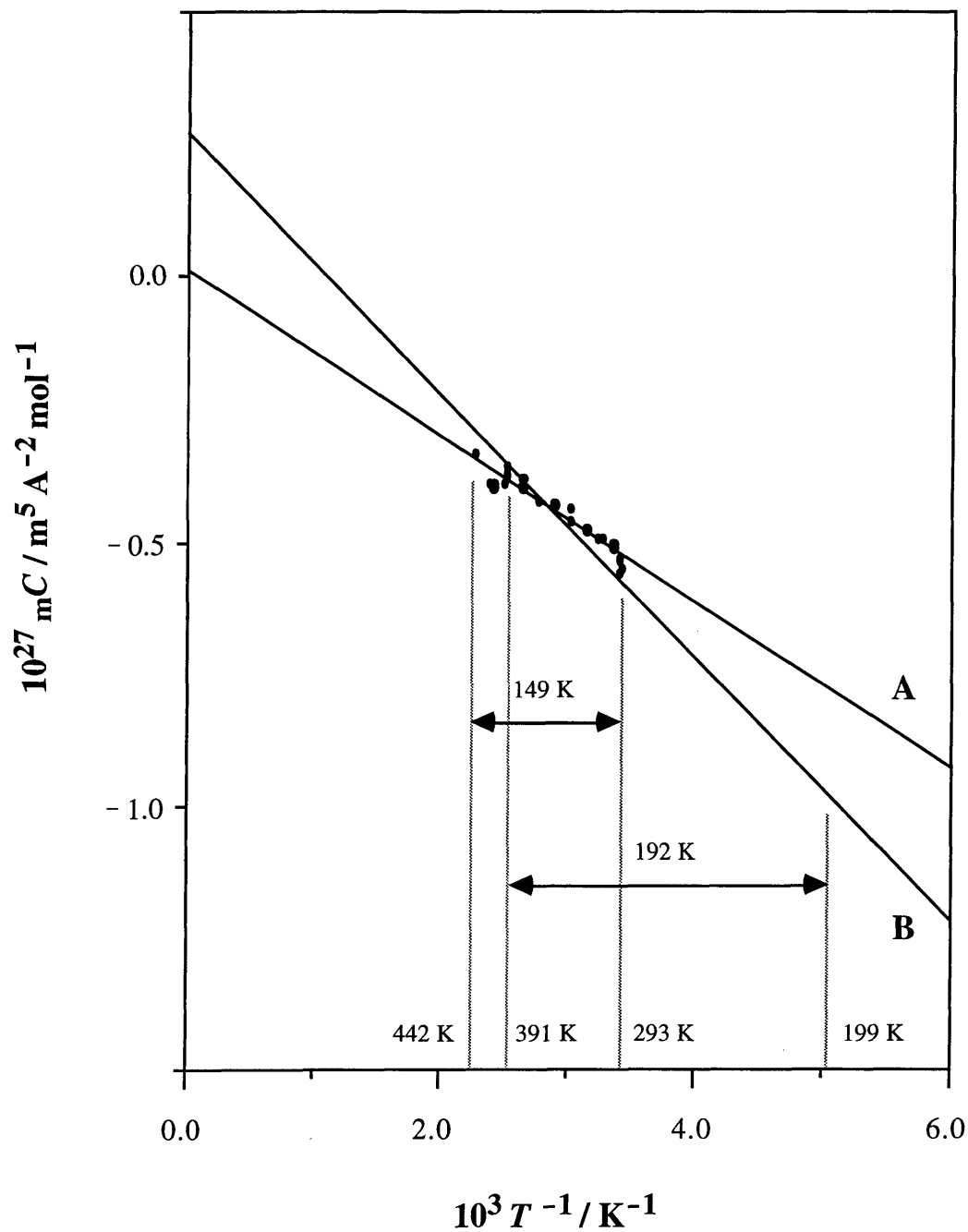


Figure 4.2 Comparison of the temperature dependences of the Cotton-Mouton effect of acetylene.

Line A, present study, with actual data points shown; line B, reference 1, without actual data points shown.

TABLE 4.2 ANALYSIS OF THE TEMPERATURE DEPENDENCE OF THE COTTON-MOUTON EFFECT OF ACETYLENE AT $\lambda = 632.8$ nm

Property	Value	Literature value
10^{27} intercept / $\text{m}^5 \text{A}^{-2} \text{mol}^{-1}$	0.011 ± 0.030	0.27 ± 0.02 (a)
10^{24} slope / $\text{m}^5 \text{A}^{-2} \text{K mol}^{-1}$	-0.157 ± 0.010	-0.248 ± 0.006 (a)
$10^{50} \Delta\eta$ / $\text{C m}^2 \text{V}^{-1} \text{T}^{-2}$	3 ± 8	68 ± 5 (a)
$10^{40} \Delta\alpha$ / $\text{C m}^2 \text{V}^{-1}$ (b)	2.072 ± 0.021	
$10^{29} \Delta\chi$ / J T^{-2}	-3.94 ± 0.25	-6.25 ± 0.16 (a)
$10^{29} \chi$ / J T^{-2} (c)	-34.5	
$10^{29} \chi_{zz}$ / J T^{-2}	-37.2	
$10^{29} \chi_{xx}$ / J T^{-2}	-33.2	
g (d)	0.04903 ± 0.00004	
B_0 / GHz (e)	35.2738	
$10^{40} \Theta$ / C m^2	20.1 ± 0.6	25.4 ± 0.3 (a)

(a) Reference 1.

(b) Reference 8.

(c) Reference 9.

(d) Reference 2.

(e) Reference 10.

For a rigid linear molecule, the quadrupole moment, Θ , can be evaluated through a rearrangement of equation (1.26):

$$\Theta = \frac{eIg}{m_p} - \left(\frac{4m_e}{e} \right) \Delta\chi \quad (4.2)$$

in which I is the moment of inertia and g is the rotational g value. The quadrupole moment was derived from equation (4.2) using the rotational g value from molecular beam magnetic resonance spectroscopy² and the magnetic anisotropy. In the evaluation of this property, it is assumed that the molecule is rigid and therefore the effects of molecular vibration are considered to be negligible.¹¹ To facilitate discussion of the results, chronological summaries of previous experimental and theoretical values of $\Delta\chi$ and Θ have been prepared as Tables 4.3 and 4.4, respectively.

In relation to the magnetic anisotropy, the difference in the slopes of the plots of ${}_mC$ against T^{-1} (Table 4.2) is such that the value of $\Delta\chi$ (in units of $10^{-29} \text{ J T}^{-2}$) determined in this study (-3.94 ± 0.25) is significantly smaller than that given by the previous investigation (-6.25 ± 0.16); the only other experimental values (Table 4.3) are indirect estimates^{12,13} that are apparently unreliable. The SCF calculation of the diamagnetic contribution to $\Delta\chi$, $\Delta\chi^d$, which defines Θ , made no allowance for correlation and vibrational effects, and the result obtained from a variant of equation (4.2) and the experimental g value is much too large in magnitude. The CHF-IGLO procedure¹⁴ for the direct calculation of $\Delta\chi$ suffers from the same deficiencies, but has been claimed to be reliable if sufficiently large basis sets are used. By contrast, the MRSDCI-ANO calculations⁵ showed that, in comparison with earlier studies, the theoretical value of Θ for acetylene is significantly reduced by both aforementioned factors (electron correlation $\approx -12\%$, vibrational anharmonicity $\approx -9\%$, total reduction $\approx -20\%$). Combination of this definitive theoretical result with the experimental g value yields, from a variant of equation (4.2), what should be a

TABLE 4.3 VALUES OF THE MAGNETIC ANISOTROPY OF ACETYLENE

Year	Method	$10^{29} \Delta\chi / \text{J T}^{-2}$	Ref.
<i>Experiment</i>			
1973	Estimated from $\Delta\chi$ values (microwave Zeeman effect) of $\text{CH}_3\text{C}\equiv\text{CH}$ and related molecules	-7.5 ± 0.8	12
1983	Temperature dependence of Cotton-Mouton effect	-6.25 ± 0.16	1
1983	Microwave Zeeman effect of $\text{HC}\equiv\text{CH-HCl}$ complex	-6.8 ± 2.3	13
1992	Temperature dependence of Cotton-Mouton effect (this study)	-3.94 ± 0.25	
<i>Theory</i>			
1979	SCF calculations of $\Delta\chi^d$ combined with experimental g value	-5.9	3
1983	CHF-IGLO calculations	-3.02, -3.75	14
1991	MRSDCI-ANO calculations of Θ (with vibrational corrections) combined with experimental g value	-3.55 ± 0.26	5

TABLE 4.4 VALUES OF THE MOLECULAR QUADRUPOLE MOMENT OF ACETYLENE

Year	Method	$10^{40} \Theta / \text{C m}^2$	Ref.
<i>Experiment</i>			
1959	Foreign-gas broadening of microwave spectral lines	10	15, 16
1967	Gas viscosities and density second virial coefficients	16.7	17
1969	Effective pair potential and reduced thermodynamic properties	14.0	18
1972	Localized atom-dipole model	18.0	19
1973	Estimated value of $\Delta\chi$ (microwave Zeeman effect of $\text{CH}_3\text{C}\equiv\text{CH}$ and related molecules) and g value	28.0 ± 3.3	12
1983	Experimental value of $\Delta\chi$ (Cotton-Mouton effect) and g value	25.4 ± 0.3	1
1983	Estimated value of $\Delta\chi$ (microwave Zeeman effect of $\text{HC}\equiv\text{CH-HCl}$ complex) and g value	26.7 ± 5.3	13
1988	Collision-induced far-infrared absorption in $\text{HC}\equiv\text{CH-Ar}$ mixtures	18.1 ± 1.4	4
1992	Single-crystal X-ray diffraction data	19.0 - 25.9	20-22

Table 4.4 continues on next page

1992	Experimental value of $\Delta\chi$ (Cotton-Mouton effect) and g value (this study)	20.1 ± 0.6	
1994	Single-temperature electric field-gradient induced birefringence	19.7 ± 1.0	23
	<i>Theory</i>		
1979	SCF calculations (result confirmed by several subsequent studies)	24.5	3, 24-28
1987	CCAMM-CISD calculations	22.1	29
1989	ACCD calculations	22.1	26
1989	MP2 calculations	20.7	30
1991	SDQ-MP4 calculations	21.9	28
1991	MRSDCI-ANO calculations (with vibrational corrections)	19.2 ± 0.5	5

reliable value of $\Delta\chi$ (-3.55 ± 0.26) which is in reasonable agreement with the present direct experimental value (-3.94 ± 0.25), when the quoted uncertainties are taken into account.

Much more attention has, to date, been given to the quadrupole moment than to the magnetic anisotropy of acetylene, and many experimental and theoretical techniques, summarized in Table 4.4, have been used to determine the magnitude and sign of this property. However, it has been recognized that early studies¹⁵⁻¹⁸ are somewhat limited and so the more recent experimental values are considered more reliable. The agreement of the result obtained from collision-induced far-infrared absorption in acetylene-argon mixtures⁴ (18.1 ± 1.4), a recent direct single-temperature measurement²³ of the quadrupole moment by the technique of electric field-gradient induced birefringence (19.7 ± 1.0), and the best theoretical prediction⁵ (19.2 ± 0.5) with the present result (20.1 ± 0.6) obtained from the temperature dependence of the Cotton-Mouton effect and the known g value, is probably as good as could reasonably be expected.

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