CHAPTER 5 - THE MOLECULAR POLARIZABILITIES OF DIMETHYL ETHER, DIMETHYL SULFIDE, OXIRANE, FURAN AND THIOPHENE

5.1 INTRODUCTION

Determinations, by experimental and theoretical methods, of accurate molecular polarizabilities and multipole moments are of considerable interest, not only because of the intrinsic value of these properties but also because their ab initio calculation is an important test of the methods of computational quantum chemistry. In this chapter, measurements of the temperature dependence of the Cotton-Mouton effect are presented and then combined with the magnetizabilities, Rayleigh depolarization ratios and mean polarizabilities to yield the optical-frequency principal polarizabilities of molecules in the series $(CH_3)_2X$, $(CH_2)_2X$ and C_4H_4X with $X = O$ and S. These results were complemented by SCF and MP2-level calculations, with the previously developed 6-31G (+sd+sp) basis set, of the mean and anisotropic optical-frequency polarizabilities.[1]

Because of the particular combination of experimental results that was used, two possible sets of the components of the polarizabilities of dimethyl ether, dimethyl sulfide, oxirane (ethylene oxide), furan and thiophene were obtained. In order to determine the correct set for each species, comparisons were made with the values derived from theoretical methods, thus highlighting one benefit of simultaneous experimental and theoretical studies.

The optical-frequency polarizabilities of furan and thiophene have previously been determined from an analysis of the molar refractions and infinite-dilution

Cotton-Mouton and Kerr constants of these species[2] but solution-state measurements do not yield polarizabilities that are applicable to free molecules, due to solute-solvent interactions, local-field corrections and assumptions about both magnetic and electric hyperpolarizabilities.

5.2 EXPERIMENTAL RESULTS

Samples used were as follows: dimethyl ether (Matheson, ≈99.9%) and oxirane (Matheson, >99.7%), used without further treatment; dimethyl sulfide (Merck, ≥ 99%), purified by fractional distillation under reduced pressure; furan (Merck, ≈98%), fractionally distilled from phosphorus pentoxide; and thiophene (Merck, ≈99%), refluxed with and fractionally distilled from sodium. The purities of dimethyl ether, dimethyl sulfide and oxirane were confirmed by gas chromatographic and mass spectrometric analyses. Errors arising from impurities were considered to be negligible. In addition, the compounds that are normally liquids (dimethyl sulfide, furan and thiophene) were subjected to several freeze-pump-thaw-distil cycles in the vapour-handling system immediately prior to the commencement of pressure-dependence measurements.

Magnetic field-induced birefringences at λ = 632.8 nm were measured over ranges of pressure and temperature, and the temperature dependences were adequately determined. Owing to the instability of thiirane (ethylene sulfide), $(CH_2)_2S$, at temperatures above room temperature, a study of the temperature dependence of the Cotton-Mouton effect was not possible. Gas densities were calculated from measured gas pressures and temperatures using published density second virial coefficients.[3] Cotton-Mouton second virial coefficients were not detectable under the conditions of the experiments. Results of measurements on these compounds are summarized in Tables 5.1, 5.2, 5.3, 5.4 and 5.5, where the uncertainties shown are based on the

TABLE 5.1 COTTON-MOUTON EFFECT OF DIMETHYL ETHER AT $\lambda = 632.8$ nm

T / K	No. of pressures	Maximum p / kPa	$10^6 B$ / m^3mol^{-1}	$10^{27}\,{}_{m}C$ / $m^5A^{-2}mol^{-1}$
414.5	9	300	-235	-0.553 ± 0.021
395.3	8	299	-256	-0.567 ± 0.034
381.5	9	300	-272	-0.633 ± 0.020
362.9	8	299	-299	-0.740 ± 0.028
340.2	11	399	-330	-0.724 ± 0.014
328.5	12	399	-365	-0.785 ± 0.027
316.5	14	488	-400	-0.768 ± 0.012
303.2	14	446	-439	-0.808 ± 0.023
298.5	12	426	-452	-0.819 ± 0.026
294.9	14	445	-463	-0.829 ± 0.010

TABLE 5.2 COTTON-MOUTON EFFECT OF DIMETHYL SULFIDE AT λ = 632.8 nm

T / K	No. of pressures	Maximum p / kPa	$10^6 B$ / $\mathrm{m^3 mol^{-1}}$	$10^{27}{}_{\mathrm{m}}C$ / $\mathrm{m^5 A^{-2} mol^{-1}}$
443.9	16	114	-378	-0.795 ± 0.034
424.1	13	117	-410	-0.857 ± 0.034
414.2	19	116	-429	-0.892 ± 0.035
404.4	9	106	-450	-0.994 ± 0.042
387.9	15	118	-490	-0.977 ± 0.049
383.6	11	98	-502	-0.973 ± 0.037
363.1	15	113	-564	-1.099 ± 0.039
341.0	10	101	-654	-1.164 ± 0.031
333.6	7	98	-686	-1.179 ± 0.048
318.2	7	40	-771	-1.234 ± 0.083
317.2	7	93	-777	-1.217 ± 0.042
301.2	12	43	-890	-1.350 ± 0.079
293.2	7	34	-955	-1.396 ± 0.126

TABLE 5.3 COTTON-MOUTON EFFECT OF OXIRANE AT $\lambda = 632.8$ nm

T / K	No. of pressures	Maximum p / kPa	$10^6 B$ / $\mathrm{m^3 mol^{-1}}$	$10^{27}\,{}_{\mathrm{m}}C$ / $\mathrm{m^5 A^{-2} mol^{-1}}$
447.6	10	101	-263	0.390 ± 0.023
420.6	13	110	-293	0.495 ± 0.049
404.6	10	100	-315	0.457 ± 0.061
379.2	13	117	-331	0.615 ± 0.033
363.6	17	108	-387	0.685 ± 0.037
351.9	9	99	-415	0.566 ± 0.087
327.0	8	116	-488	0.602 ± 0.050
326.8	14	117	-489	0.616 ± 0.047
325.2	8	109	-493	0.722 ± 0.041
307.3	9	120	-566	0.830 ± 0.048
306.2	9	109	-571	0.715 ± 0.043
302.3	15	136	-585	0.796 ± 0.066
302.1	18	129	-586	0.776 ± 0.047
293.6	14	118	-636	0.901 ± 0.071
292.7	7	100	-640	0.755 ± 0.041

TABLE 5.4 COTTON-MOUTON EFFECT OF FURAN AT $\lambda = 632.8$ nm

T / K	No. of pressures	Maximum p / kPa	$10^6 B$ / m^3mol^{-1}	$10^{27}{}_{m}C$ / $m^5A^{-2}mol^{-1}$
445.0	6	55	-372	10.09 ± 0.07
444.7	4	55	-372	10.00 ± 0.02
419.4	5	42	-410	10.55 ± 0.14
384.7	5	55	-479	11.68 ± 0.07
351.5	5	55	-572	12.52 ± 0.04
326.9	6	55	-667	13.55 ± 0.06
307.1	5	53	-770	14.44 ± 0.12
294.6	6	55	-851	14.89 ± 0.04

TABLE 5.5 COTTON-MOUTON EFFECT OF THIOPHENE AT $\lambda = 632.8$ nm

T / K	No. of pressures	Maximum p / kPa	$10^6 B$ / $\mathrm{m^3 mol^{-1}}$	$10^{27}\,{}_{\mathrm{m}}C$ / $\mathrm{m^5 A^{-2} mol^{-1}}$
446.0	6	23.1	-587	18.9 ± 0.2
408.5	6	24.3	-685	20.6 ± 0.2
384.3	7	25.8	-770	22.3 ± 0.3
373.1	6	20.2	-817	23.0 ± 0.2
350.6	5	22.3	-930	23.6 ± 0.2
325.8	7	20.4	-1100	26.0 ± 0.2
315.3	6	7.7	-1185	26.4 ± 0.5
294.1	7	6.8	-1405	28.1 ± 0.4

standard deviations derived from least-squares straight lines. Previous studies of these molecules, and their selenium analogues, are limited to measurements of the solution-phase Cotton-Mouton constants of furan, thiophene and selenophene dissolved in cyclohexane.[2]

5.3 ANALYSIS AND DISCUSSION

The temperature dependence of ${}_{\mathrm{m}}C$ for molecules of $C_{2\mathrm{v}}$ or higher symmetry can be described by the equation

$${}_{\mathrm{m}}C = \left(\frac{N_{\mathrm{A}}\mu_0^{2}}{270\varepsilon_0}\right)\left\{\Delta\eta + \frac{1}{kT}\left[\alpha_{xx}(\chi_{xx}-\chi) + \alpha_{yy}(\chi_{yy}-\chi) + \alpha_{zz}(\chi_{zz}-\chi)\right]\right\} \qquad (5.1)$$

in which $\Delta\eta\left(=\eta_{\alpha\beta:\alpha\beta} - \frac{1}{3}\eta_{\alpha\alpha:\beta\beta}\right)$ is the anisotropy in the magnetic hyperpolarizability; α_{xx}, α_{yy}, α_{zz} and χ_{xx}, χ_{yy}, χ_{zz} are the diagonal elements of the optical-frequency polarizability and the magnetizability, respectively; and $\chi\left(=\frac{1}{3}\chi_{\alpha\alpha}\right)$ is the mean magnetizability. The molecular axes, shown in Figure 5.1, are defined such that x and y are directions in the plane of the heavy atoms (for furan and thiophene, the ring lies in the xy plane), x is coincident with the direction (- to +) of the molecular dipole moment, and z is orthogonal to both x and y. The components of the polarizability can be related to the isotropic refractive index, n, and the Rayleigh depolarization ratio, ρ_0, by the following equations

$$(2V_{\mathrm{m}}\varepsilon_0/N_{\mathrm{A}})(n-1) \;=\; \alpha \;=\; \frac{1}{3}\left(\alpha_{xx}+\alpha_{yy}+\alpha_{zz}\right) \qquad (5.2)$$

$$\begin{aligned} 5\rho_0(3-4\rho_0)^{-1} &= \kappa^2 \\ &= \left[\left(\alpha_{xx}-\alpha_{yy}\right)^2 + \left(\alpha_{yy}-\alpha_{zz}\right)^2 + \left(\alpha_{zz}-\alpha_{xx}\right)^2\right]\Big/18\alpha^2 \end{aligned} \qquad (5.3)$$

so that simultaneous solution of equations (5.1) - (5.3), in conjunction with the known magnetizabilities and the mean polarizability, yields two sets of possible principal polarizabilities.

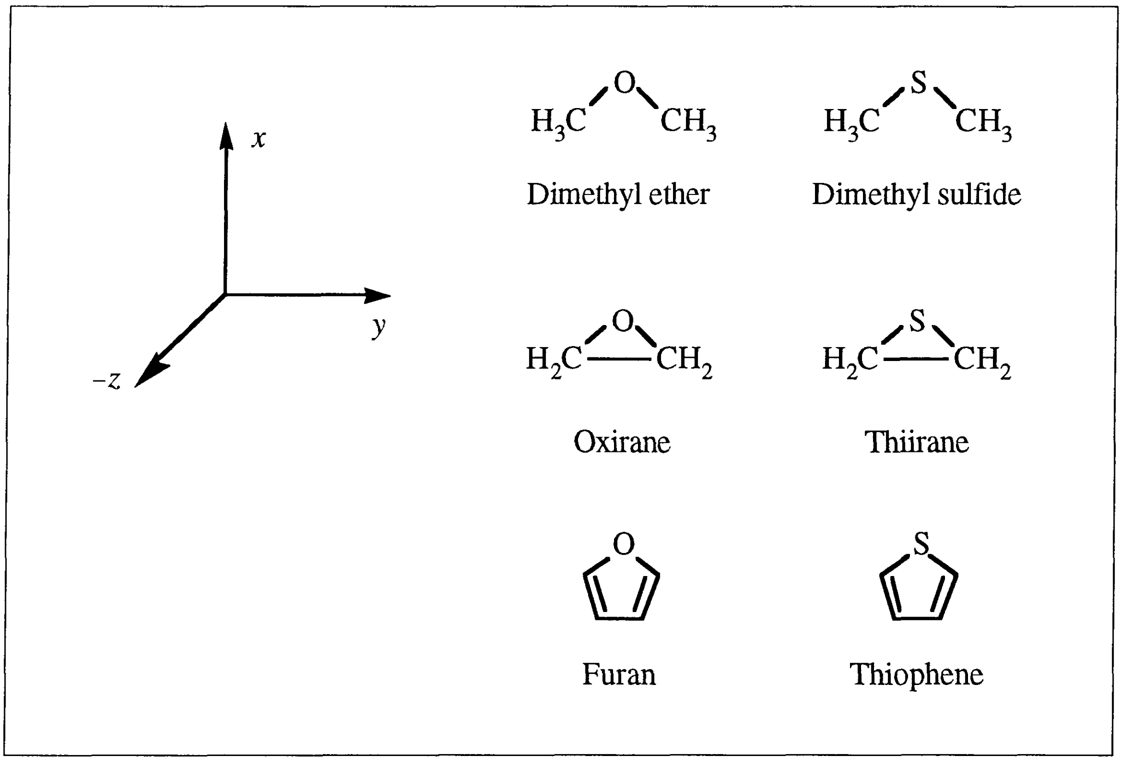


Figure 5.1: Molecular axes of dimethyl ether, dimethyl sulfide, oxirane, thiirane, furan and thiophene.

The linear dependence of ${}_{\mathrm{m}}C$ on T^{-1} predicted by equation (5.1) was observed in each case and is shown in Figures 5.2, 5.3 and 5.4, and Tables 5.6, 5.7, 5.8, 5.9 and 5.10 contain the intercepts and slopes of the least-squares straight lines, together with values of the magnetic hyperpolarizability anisotropy, magnetizabilities, mean polarizabilities, Rayleigh depolarization ratios and the derived molecular polarizabilities.

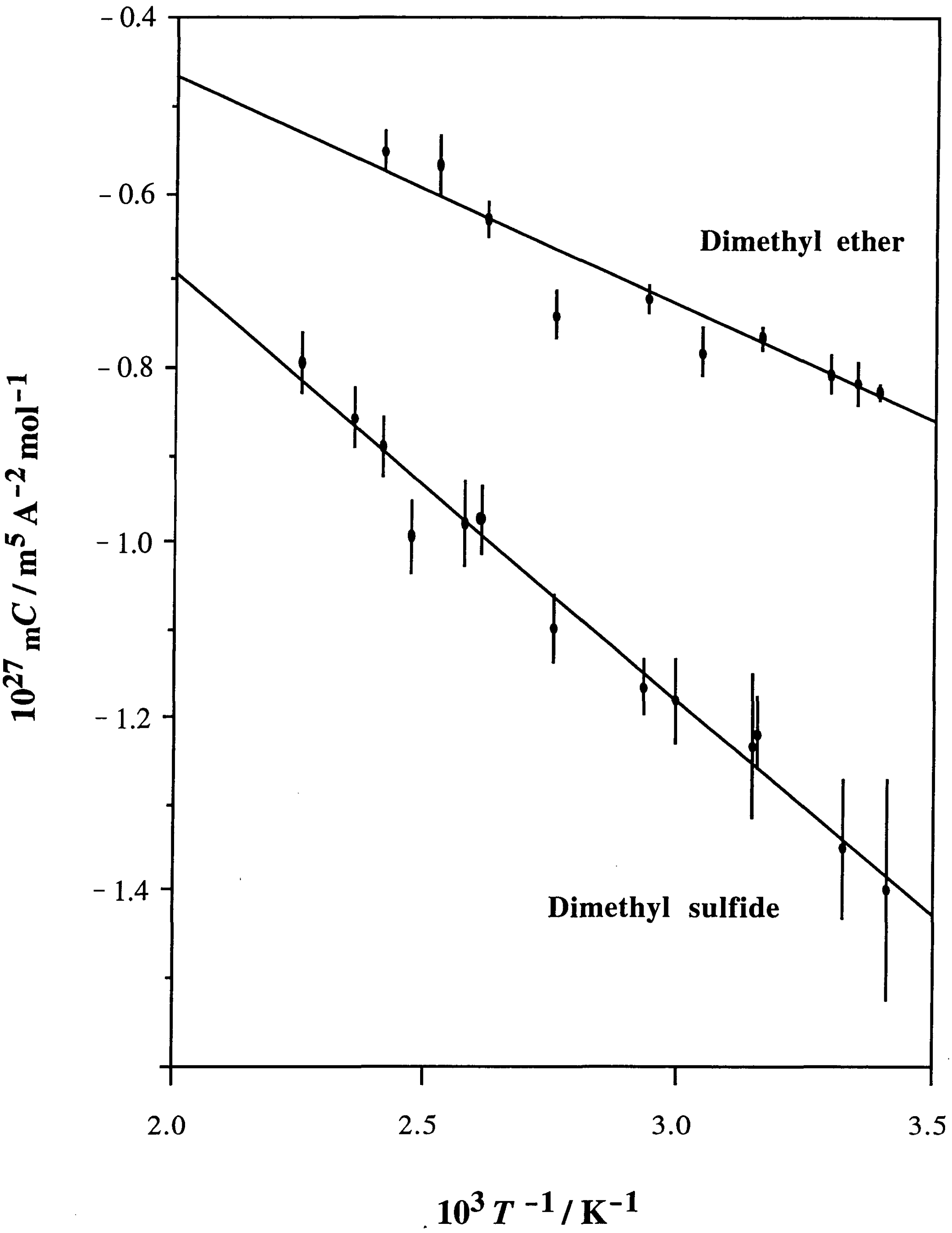


Figure 5.2: Temperature dependence of the Cotton-Mouton constants of dimethyl ether and dimethyl sulfide.

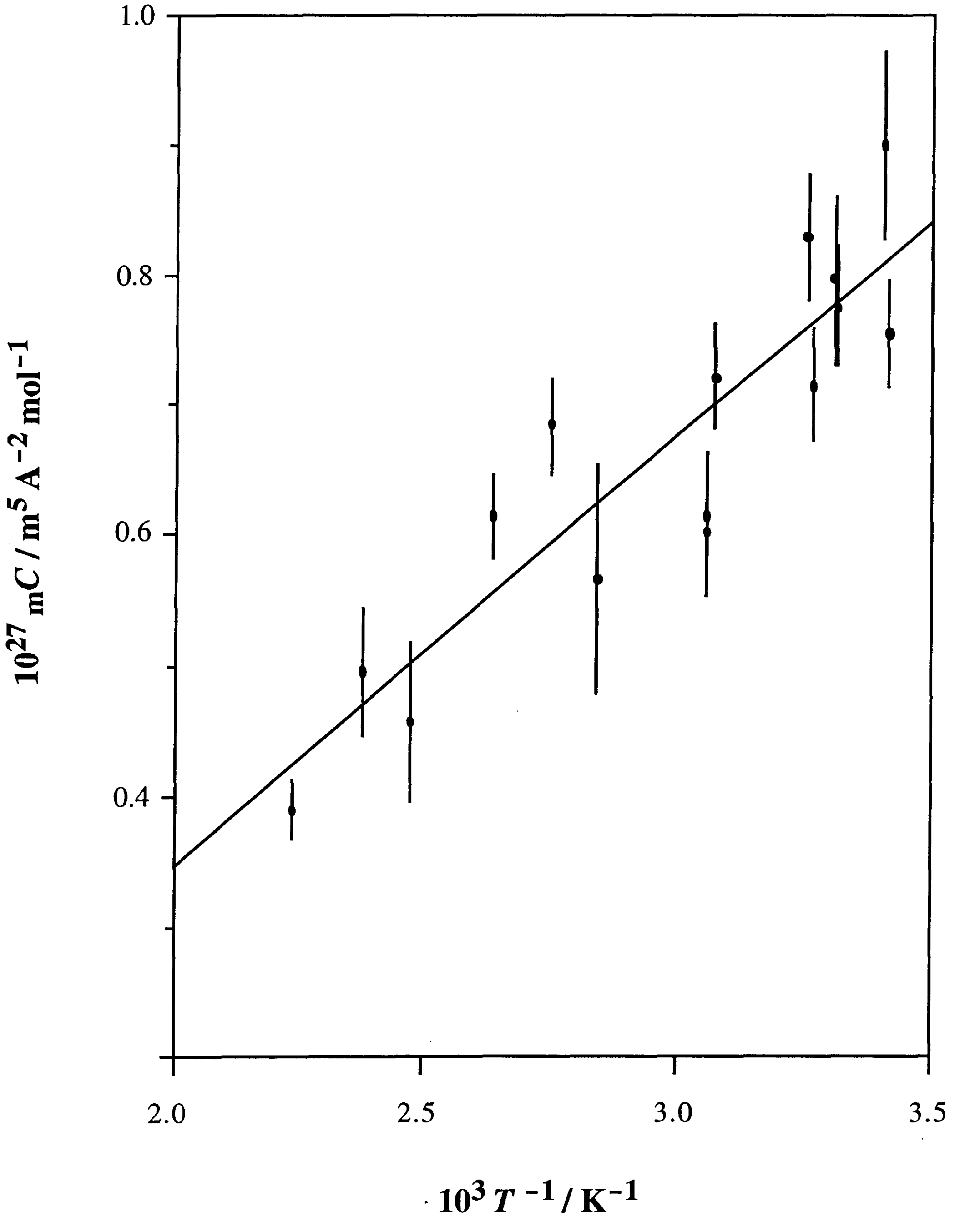


Figure 5.3: Temperature dependence of the Cotton-Mouton constant of oxirane.

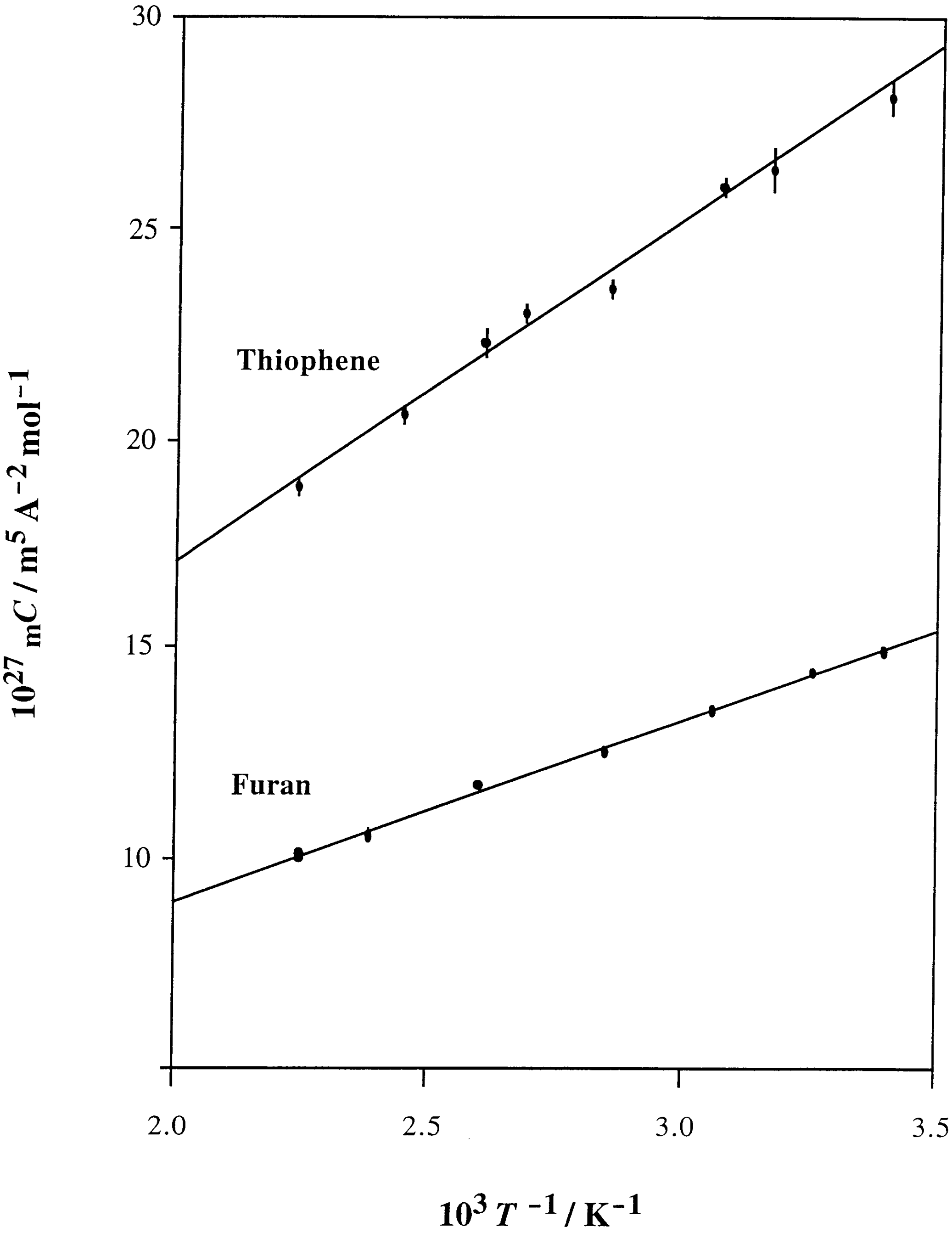


Figure 5.4: Temperature dependence of the vapour-phase Cotton-Mouton constants of furan and thiophene.

TABLE 5.6 ANALYSIS OF THE TEMPERATURE DEPENDENCE OF THE COTTON-MOUTON EFFECT OF DIMETHYL ETHER AT $\lambda = 632.8$ nm

Property	Value	
10^{27}intercept / $\mathrm{m^5A^{-2}mol^{-1}}$	0.052 ± 0.069	
10^{24}slope / $\mathrm{m^5A^{-2}K\,mol^{-1}}$	-0.261 ± 0.022	
$10^{50}\Delta\eta$ / $\mathrm{C\,m^2V^{-1}T^{-2}}$	13 ± 17	
$10^{29}(\chi_{xx}-\chi)$ / $\mathrm{J\,T^{-2}}$	0.66 ± 0.33 (a)	
$10^{29}(\chi_{yy}-\chi)$ / $\mathrm{J\,T^{-2}}$	-5.76 ± 0.39 (a)	
$10^{29}(\chi_{zz}-\chi)$ / $\mathrm{J\,T^{-2}}$	-5.09 ± 0.51 (a)	
$10^{40}\alpha$ / $\mathrm{C\,m^2V^{-1}}$	5.81 ± 0.06 (b)	
$10^{2}\rho_0$	0.35 ± 0.06 (b)	
	Set One	Set Two
$10^{40}\alpha_{xx}$ / $\mathrm{C\,m^2V^{-1}}$	6.29 ± 0.48	5.19 ± 0.40
$10^{40}\alpha_{yy}$ / $\mathrm{C\,m^2V^{-1}}$	6.17 ± 0.54	6.60 ± 0.22
$10^{40}\alpha_{zz}$ / $\mathrm{C\,m^2V^{-1}}$	4.97 ± 0.12	5.64 ± 0.60

(a) Reference 4. (b) Reference 5.

TABLE 5.7 ANALYSIS OF THE TEMPERATURE DEPENDENCE OF THE COTTON-MOUTON EFFECT OF DIMETHYL SULFIDE AT $\lambda = 632.8$ nm

Property	Value	
10^{27}intercept / $\mathrm{m^5A^{-2}mol^{-1}}$	0.13 ± 0.10	
10^{24}slope / $\mathrm{m^5A^{-2}K\,mol^{-1}}$	-0.434 ± 0.038	
$10^{50}\Delta\eta$ / $\mathrm{C\,m^2V^{-1}T^{-2}}$	33 ± 26	
$10^{29}(\chi_{xx}-\chi)$ / $\mathrm{J\,T^{-2}}$	-1.39 ± 0.16 (a)	
$10^{29}(\chi_{yy}-\chi)$ / $\mathrm{J\,T^{-2}}$	-2.51 ± 0.19 (a)	
$10^{29}(\chi_{zz}-\chi)$ / $\mathrm{J\,T^{-2}}$	3.91 ± 0.25 (a)	
$10^{40}\alpha$ / $\mathrm{C\,m^2V^{-1}}$	8.40 ± 0.08 (b)	
$10^{2}\rho_0$	0.506 ± 0.015 (c)	
	Set One	Set Two
$10^{40}\alpha_{xx}$ / $\mathrm{C\,m^2V^{-1}}$	9.36 ± 0.26	8.56 ± 0.18
$10^{40}\alpha_{yy}$ / $\mathrm{C\,m^2V^{-1}}$	9.07 ± 0.16	9.72 ± 0.22
$10^{40}\alpha_{zz}$ / $\mathrm{C\,m^2V^{-1}}$	6.90 ± 0.10	7.04 ± 0.12

(a) Reference 6. (b) Reference 5. (c) References 1 and 7.

TABLE 5.8 ANALYSIS OF THE TEMPERATURE DEPENDENCE OF THE COTTON-MOUTON EFFECT OF OXIRANE AT $\lambda = 632.8$ nm

Property	Value	
10^{27}intercept / $\mathrm{m^5A^{-2}mol^{-1}}$	-0.33 ± 0.10	
10^{24}slope / $\mathrm{m^5A^{-2}K\,mol^{-1}}$	0.336 ± 0.035	
$10^{50}\Delta\eta$ / $\mathrm{C\,m^2V^{-1}T^{-2}}$	-83 ± 25	
$10^{29}(\chi_{xx}-\chi)$ / $\mathrm{J\,T^{-2}}$	-0.03 ± 0.06 (a)	
$10^{29}(\chi_{yy}-\chi)$ / $\mathrm{J\,T^{-2}}$	10.22 ± 0.04 (a)	
$10^{29}(\chi_{zz}-\chi)$ / $\mathrm{J\,T^{-2}}$	-10.19 ± 0.07 (a)	
$10^{40}\alpha$ / $\mathrm{C\,m^2V^{-1}}$	4.91 ± 0.05 (b)	
$10^{2}\rho_0$	0.295 ± 0.010 (b)	
	Set One	Set Two
$10^{40}\alpha_{xx}$ / $\mathrm{C\,m^2V^{-1}}$	5.11 ± 0.30	4.71 ± 0.28
$10^{40}\alpha_{yy}$ / $\mathrm{C\,m^2V^{-1}}$	5.38 ± 0.26	5.58 ± 0.09
$10^{40}\alpha_{zz}$ / $\mathrm{C\,m^2V^{-1}}$	4.24 ± 0.10	4.44 ± 0.28

(a) Reference 8. (b) Reference 5.

TABLE 5.9 ANALYSIS OF THE TEMPERATURE DEPENDENCE OF THE COTTON-MOUTON EFFECT OF FURAN AT $\lambda = 632.8$ nm

Property	Value	
10^{27}intercept / $m^5A^{-2}mol^{-1}$	0.38 ± 0.12	
10^{24}slope / $m^5A^{-2}K\ mol^{-1}$	4.28 ± 0.05	
$10^{50}\Delta\eta$ / $C\,m^2V^{-1}T^{-2}$	96 ± 31	
$10^{29}(\chi_{xx}-\chi)$ / $J\,T^{-2}$	23.82 ± 0.13 (a)	
$10^{29}(\chi_{yy}-\chi)$ / $J\,T^{-2}$	19.04 ± 0.11 (a)	
$10^{29}(\chi_{zz}-\chi)$ / $J\,T^{-2}$	-42.86 ± 0.17 (a)	
$10^{40}\alpha$ / $C\,m^2V^{-1}$	8.10 ± 0.08 (b)	
$10^{2}\rho_0$	1.31 ± 0.02 (c)	
	Set One	Set Two
$10^{40}\alpha_{xx}$ / $C\,m^2V^{-1}$	9.98 ± 0.39	8.79 ± 0.37
$10^{40}\alpha_{yy}$ / $C\,m^2V^{-1}$	8.48 ± 0.26	9.76 ± 0.42
$10^{40}\alpha_{zz}$ / $C\,m^2V^{-1}$	5.85 ± 0.19	5.75 ± 0.13

(a) Reference 9. (b) Reference 2.

(c) References 1 and 7.

TABLE 5.10 ANALYSIS OF THE TEMPERATURE DEPENDENCE OF THE COTTON-MOUTON EFFECT OF THIOPHENE AT $\lambda = 632.8$ nm

Property	Value	
10^{27}intercept / $\mathrm{m^5A^{-2}mol^{-1}}$	0.72 ± 1.01	
10^{24}slope / $\mathrm{m^5A^{-2}K\,mol^{-1}}$	8.16 ± 0.37	
$10^{50}\Delta\eta$ / $\mathrm{C\,m^2V^{-1}T^{-2}}$	180 ± 250	
$10^{29}(\chi_{xx}-\chi)$ / $\mathrm{J\,T^{-2}}$	27.45 ± 0.61 [a]	
$10^{29}(\chi_{yy}-\chi)$ / $\mathrm{J\,T^{-2}}$	28.01 ± 0.72 [a]	
$10^{29}(\chi_{zz}-\chi)$ / $\mathrm{J\,T^{-2}}$	-55.46 ± 0.94 [a]	
$10^{40}\alpha$ / $\mathrm{C\,m^2V^{-1}}$	10.69 ± 0.11 [b]	
$10^{2}\rho_0$	1.58 ± 0.02 [c]	
	Set One	Set Two
$10^{40}\alpha_{xx}$ / $\mathrm{C\,m^2V^{-1}}$	11.65 ± 1.03	13.11 ± 0.81
$10^{40}\alpha_{yy}$ / $\mathrm{C\,m^2V^{-1}}$	13.13 ± 0.81	11.68 ± 1.02
$10^{40}\alpha_{zz}$ / $\mathrm{C\,m^2V^{-1}}$	7.29 ± 0.47	7.29 ± 0.46

[a] Reference 9. [b] Reference 2.

[c] References 1 and 7.

As with previous studies of other medium-sized species, the values of the magnetic hyperpolarizability anisotropy are somewhat imprecisely determined by experiments of this kind. However, it is of interest to note that the proportion of the Cotton-Mouton constant at 298 K that originates in the temperature-independent contribution appears unusually large for $(CH_2)_2O$ ($\approx -40 \pm 15\%$) but typically smaller for $(CH_3)_2O$, $(CH_3)_2S$, C_4H_4O, and C_4H_4S ($\approx -6 \pm 9\%$, $\approx -10 \pm 8\%$, $\approx -3 \pm 1\%$ and $\approx -3 \pm 4\%$); apart from $(CH_2)_2O$, these contributions are similar to those described elsewhere in this thesis and in other studies.[10]

For three of the molecules studied, oxirane, furan and thiophene, simultaneous solutions of equations (5.1) - (5.3) were straightforward but, for dimethyl ether and dimethyl sulfide, it was necessary to vary the less precise parameters (the slope and the magnetizabilities) through the ranges defined by the quoted uncertainties, so as to obtain real solutions. A similar procedure was used, for oxirane, furan and thiophene, to estimate the likely errors in the derived polarizabilities; for dimethyl ether and dimethyl sulfide, the error was taken to be double the standard deviation resulting from the mean of real solutions. These steps were repeated for dimethyl sulfide, using alternative and earlier values of the components of the magnetizability,[4] with results insignificantly different, within the cited errors, from those quoted here.

To resolve the ambiguity arising from the two sets of principal polarizabilities obtained from the simultaneous solution of equations (5.1) - (5.3), due to the quadratic dependence of ρ_0 on the polarizability, it has often been necessary to invoke qualitative arguments, for example, bond-additivity models. In this study, instead, high-level ab initio calculations, described below, have served to discriminate between the alternatives, and no ambiguity remains.

SCF and MP2 values of static and optical-frequency polarizabilities for molecules in the $(CH_2)_2X$ and $(CH_3)_2X$ series calculated by Spackman[1] using the 6-31G (+sd + sp) basis set for C, O and S were available and, as the interest lies in the comparison of experiment and theory, only the optical-frequency (λ = 632.8 nm) polarizabilities were considered. Optical-frequency polarizabilities were obtained at the SCF level by a time-dependent coupled Hartree-Fock procedure and at the MP2 level by the addition of the SCF-level dispersion correction to the MP2-level static polarizability. This approach has previously been used by others[11] and has been shown to be a reliable method.

One of the molecules studied here, dimethyl ether, has previously been examined by a well-established and independent method that involves analysis of measurements of the temperature dependence of the Kerr effect, instead of the Cotton-Mouton effect, in conjunction with the Rayleigh depolarization ratio and mean polarizability of the species.[12] The study yielded a definitive value of α_{xx}, whilst the other two components of the polarizability, which were derived from a quadratic equation, could not be unambiguously assigned to the *y*- and *z*- directions, although it was proposed that α_{yy} should be greater than α_{zz} since the C–O bond is considered to be more polarizable along its axis than perpendicular to it.[13] The polarizabilities (expressed as $10^{40}\alpha_{xx} / \mathrm{C\,m^2V^{-1}}$, *etc.*) that were so derived (5.28 ± 0.13, 6.69 ± 0.17, 5.46 ± 0.14) are in excellent agreement with those labelled Set Two in Table 5.6. While the precision appears to be slightly higher in the earlier results, it should be noted that, in favourable circumstances,[14] the Kerr effect method provides a direct determination of α_{xx} and that the Cotton-Mouton effect method propagates the relatively large uncertainties associated with the microwave Zeeman effect magnetizabilities. On the other hand, the temperature dependence of the Kerr effect is more complicated than that of the Cotton-Mouton effect (of a diamagnetic molecule), and additional information (such as an estimate of the Kerr second hyperpolarizability, γ^K, from, for instance, electric second harmonic generation measurements) is usually required.

It has been established that the 6-31G(+sd+sp) basis set, which was specifically developed for such calculations,[15] yields MP2-level mean and anisotropic optical-frequency (λ = 623.8 nm) polarizabilities that are only about 5% smaller than experimental values, and it is believed that the components of the polarizabilities of dimethyl ether, dimethyl sulfide, oxirane, furan and thiophene are the best available theoretical estimates of these quantities. For dimethyl ether, the MP2 results at λ = 632.8 nm shown in Table 5.11 are in excellent agreement with the corresponding experimental values, being consistently below the latter values by several percent for each component. The slight discrepancy can probably be attributed to the effects of vibrational averaging, neglected in the calculations, which, when induced, can lead to increases of several percent in the individual components.[16] If the calculated principal polarizabilities for each molecule are scaled by the ratio (typically ≈ 1.02–1.06) of the experimental to the calculated mean polarizability, scaled theoretical polarizabilities that are in excellent agreement with the experimental results are obtained, thereby resolving the ambiguities in the assignment of the experimentally determined polarizabilities for dimethyl sulfide, oxirane, furan and thiophene. In particular, for oxirane, the analysis of the slope of the temperature dependence of the Cotton-Mouton effect in conjunction with the mean polarizability and the Rayleigh depolarization ratio yielded two possible sets of polarizability components. Intuitively, one would expect $\alpha_{yy} > \alpha_{xx}$, but this was of little help in deciding which set of polarizabilities is correct as both sets show the greatest polarizability along the y- axis. The scaled MP2 polarizability components are in exceptional agreement with those labelled Set Two in Table 5.8 hence it is believed that the MP2 results distinguish between the experimental alternatives. It follows, therefore, that the scaled theoretical polarizabilities for $(CH_2)_2S$, for which experimental values of the

TABLE 5.11 CALCULATED AND EXPERIMENTAL OPTICAL-FREQUENCY (λ = 632.8 nm) POLARIZABILITIES[a] OF $(CH_3)_2X$, $(CH_2)_2X$, AND C_4H_4X (X = O, S)

	calc[b]			calc[b]		
	MP2	scaled	expt	MP2	scaled	expt
		$(CH_3)_2O$			$(CH_3)_2S$	
α_{xx}	5.18	5.47	5.19 ± 0.40	8.04	8.36	8.56 ± 0.18
α_{yy}	6.32	6.68	6.60 ± 0.22	9.42	9.79	9.72 ± 0.22
α_{zz}	4.99	5.28	5.64 ± 0.60	6.78	7.05	7.04 ± 0.12
α	5.50		5.81[c]	8.08		8.40[c]
		$(CH_2)_2O$			$(CH_2)_2S$	
α_{xx}	4.41	4.64	4.71 ± 0.28	8.66	9.12	
α_{yy}	5.34	5.63	5.58 ± 0.09	7.03	7.41	
α_{zz}	4.23	4.46	4.44 ± 0.28	6.21	6.54	
α	4.66		4.91[c]	7.30		7.69 ± 0.08[d]
		C_4H_4O			C_4H_4S	
α_{xx}	8.68	8.91	8.79 ± 0.28	12.64	12.9	13.1 ± 0.8
α_{yy}	9.47	9.72	9.76 ± 0.09	11.29	12.0	11.7 ± 1.0
α_{zz}	5.52	5.67	5.75 ± 0.28	6.83	7.22	7.28 ± 0.46
α	7.89		8.10 ± 0.08[d]	10.16		10.7 ± 0.1[d]

[a] Polarizabilities expressed as $10^{40}\alpha_{xx}$ / C m^2V^{-1}, *etc.*

[b] Reference 1. [c] Reference 5. [d] References 1 and 7.

principal polarizabilities are not available, can be considered to be of high accuracy.[1] The theoretical calculations[1] were also extended to the selenium analogues, that is, $(CH_3)_2Se$, $(CH_2)_2Se$ and C_4H_4Se, for which such experimental values are not available.

As mentioned above, analysis of measurements[2] of the molar refractions and infinite-dilution molar Cotton-Mouton and Kerr constants of furan and thiophene as solutes in cyclohexane at λ = 632.8 nm has yielded the polarizabilities of these species as shown in Table 5.12. While these solution-state polarizabilities are not rigorously applicable to free molecules, the agreement between the polarizabilities in Table 5.12 and those labelled Set Two in Tables 5.9 and 5.10 is reasonable. Nevertheless, the relative magnitudes of the solution-state polarizability components of furan and thiophene should roughly approximate the relative magnitudes of the corresponding gas-phase values. The relationship between the components of the solution-state polarizability of furan is $\alpha_{yy} > \alpha_{xx} > \alpha_{zz}$ and this is also the case with the values chosen in this work labelled Set Two, unlike those labelled Set One, in Table 5.9. Similarly, the relationship between the components of the solution-state polarizability of thiophene is $\alpha_{xx} > \alpha_{yy} > \alpha_{zz}$, and this is in agreement with the values in Set Two, and in disagreement with those in Set One, in Table 5.10. This comparison supports the choice previously made using the theoretical values.

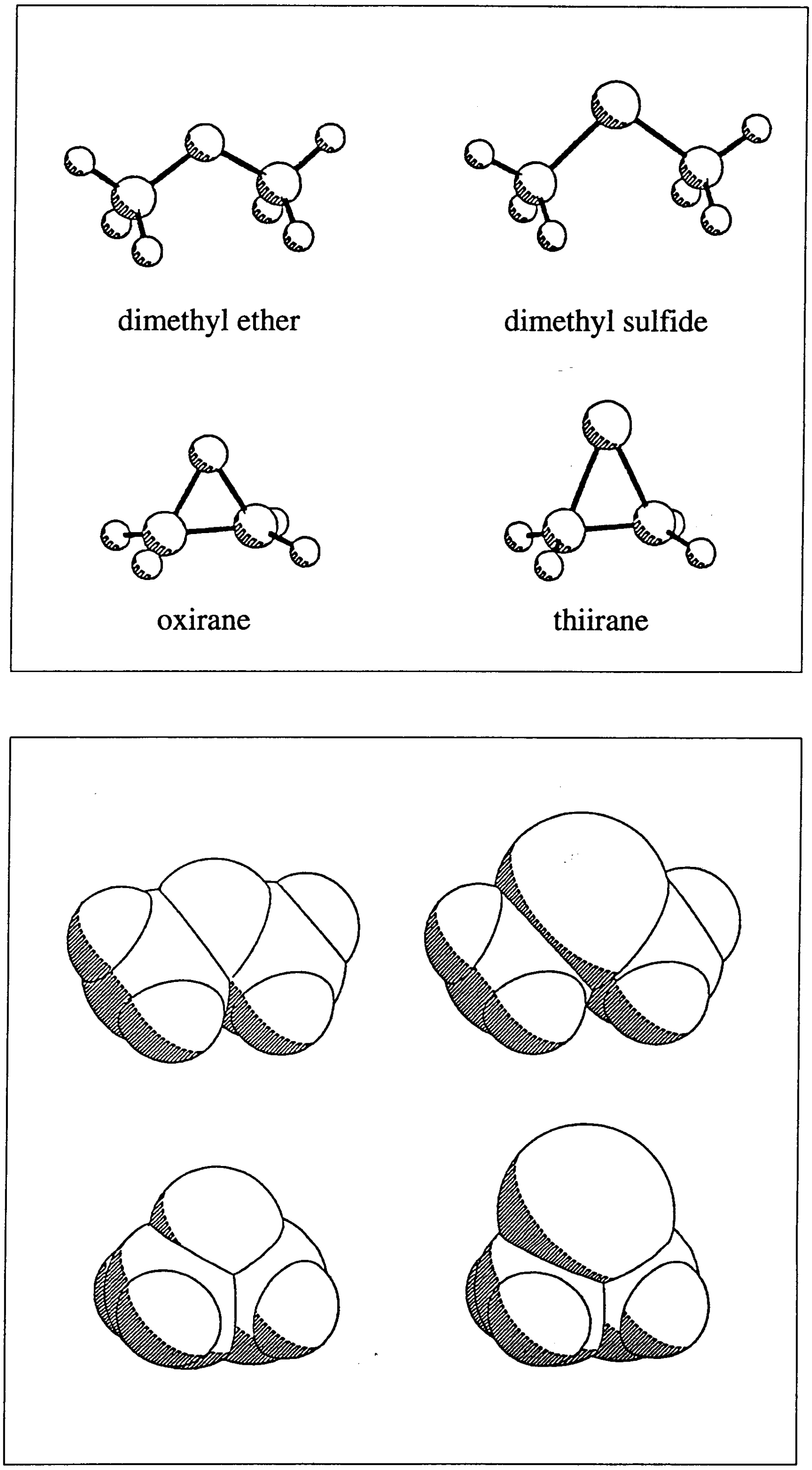
Finally, it is of interest to consider the relative magnitudes of the two in-plane components of the polarizability. It is apparent that replacement of oxygen with sulfur results in an increase in each of the principal polarizabilities, as expected. In the $(CH_3)_2X$ series the relationship is uniformly $\alpha_{xx} < \alpha_{yy}$; but in the closed-ring compounds of the $(CH_2)_2X$ and C_4H_4X series it is $\alpha_{xx} < \alpha_{yy}$ for X = O but $\alpha_{xx} > \alpha_{yy}$ for X = S. This apparent anomaly presumably originates in the shapes of the molecules, and plots of van der Waals surfaces for dimethyl ether, dimethyl

TABLE 5.12 POLARIZABILITIES OF FURAN AND THIOPHENE AS SOLUTES IN CYCLOHEXANE AT $\lambda = 632.8$ nm [(a)]

	Furan	Thiophene
$10^{40}\alpha_{xx}$ / C m^{2}V^{-1}	8.79 ± 0.24	12.63 ± 0.24
$10^{40}\alpha_{yy}$ / C m^{2}V^{-1}	9.09 ± 0.54	11.05 ± 0.53
$10^{40}\alpha_{zz}$ / C m^{2}V^{-1}	6.43 ± 0.30	8.56 ± 0.29

[(a)] Reference 2.

sulfide, oxirane and thiirane at the 6-31G(+sd+sp) geometries used for the theoretical calculations are shown in Figure 5.5.[1] These plots graphically demonstrate that for thiirane the long axis of the molecule is coincident with the bisector of the angle subtended by the heavy atoms, whereas it is perpendicular to that axis for the other three molecules. The same applies in the cases of C_4H_4O and C_4H_4S, in that the ratio of the length of the molecule along the x- axis to the y- axis is larger for furan than for thiophene due to the smaller size of oxygen compared to sulfur. For oxirane, the values of α_{yy} and α_{zz} are smaller than the corresponding polarizabilities for dimethyl ether; a similar trend is observed for thiirane and dimethyl sulfide. However, the value of α_{xx} for dimethyl sulfide is slightly smaller than that predicted for thiirane and this can be attributed to the particular orientation of the long axis of thiirane.



<u>Figure 5.5:</u> Ball and stick models and van der Waals surfaces for dimethyl ether, dimethyl sulfide, oxirane and thiirane at 6-31G (+sd + sp) geometries.

In summary, the free-molecule principal polarizabilities of dimethyl sulfide, oxirane, furan and thiophene have been determined for the first time, and re-determined for dimethyl ether, from the temperature dependence of the Cotton-Mouton effects in conjunction with other experimental data. Ambiguity in the results, due to the quadratic dependence of the Rayleigh depolarization ratio on components of the polarizability, was resolved by comparison with ab initio polarizabilities and, where available, values obtained from either other gas-phase or solution-state studies. In addition, the experimentally and theoretically determined polarizabilities of these molecules have been compared and contrasted.

5.4 REFERENCES

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CHAPTER 6 - THE MAGNETIC ANISOTROPIES OF CARBON DIOXIDE, CARBONYL SULFIDE AND CARBON DISULFIDE

6.1 INTRODUCTION

Carbon dioxide, carbonyl sulfide and carbon disulfide have attracted considerable interest from experimental and theoretical chemists in relation to their magnetic anisotropies and molecular quadrupole moments. The microwave Zeeman effect method of obtaining free-molecule magnetic anisotropies is inapplicable to non-dipolar molecules and, therefore, the Cotton-Mouton effect provides an alternative route to the magnetic anisotropy, provided the polarizability anisotropy is reliably known. However, most previous magnetic birefringence studies have assumed that temperature-independent contributions are negligible at normal temperatures, and the derived magnetic anisotropies may therefore be uncertain. Clearly, studies of the temperature dependence are necessary to obtain reliable values of both the temperature-independent magnetic hyperpolarizability anisotropy and the magnetic anisotropy. This study was undertaken in order to provide definitive values for the magnetic anisotropies of carbon dioxide, carbonyl sulfide and carbon disulfide, to compare these values with those of another group,[1] and to obtain values of the quadrupole moments of these molecules.

6.2 EXPERIMENTAL RESULTS

The sources and purities of the samples used were as follows: carbon dioxide (C.I.G. industrial grade, >99.9%) used without further purification; carbonyl sulfide

(Matheson, >97.5%) used without further purification; carbon disulfide (Fluka spectroscopic grade, >99.5%), fractionally distilled from phosphorus pentoxide, purity >99.8%. Each compound was analyzed by gas chromatography to determine the sample purity and to ensure that the impurities were negligible. The sample of carbon disulfide was subjected to several freeze-pump-thaw-distil cycles prior to the commencement of each set of pressure-dependence measurements.

Measurements of the magnetic field-induced birefringence at $\lambda = 632.8$ nm for these compounds were made at many temperatures ($\approx$293-489 K) and, at each temperature, over a range of pressures (up to $\approx$ 1100 kPa). Gas densities for carbon dioxide and carbon disulfide were calculated from measured temperatures and gas pressures using published values of the density second virial coefficients.[2] No virial coefficients were available for carbonyl sulfide, and van der Waals coefficients[3] were used instead; the correction from the ideal gas law was <2%, so that any error arising from this procedure is expected to be very small. The observed retardances were particularly large for each of these substances, and ${}_{\mathrm{m}}C$ values were obtained to high precision. Results of measurements are summarized in Tables 6.1, 6.2 and 6.3, where the uncertainties shown are based on the standard deviations derived from least-squares straight lines.

6.3 ANALYSIS AND DISCUSSION

For a linear molecule, the temperature dependence of ${}_{\mathrm{m}}C$ is described by equation (1.7):

$$ {}_{\mathrm{m}}C = \frac{N_{\mathrm{A}}\mu_0^2}{270\varepsilon_0}\left(\Delta\eta + \frac{2\Delta\alpha\Delta\chi}{3kT}\right) \qquad (6.1) $$

TABLE 6.1 COTTON-MOUTON EFFECT OF CARBON DIOXIDE AT $\lambda = 632.8$ nm

T / K	No. of pressures	Maximum p / kPa	$10^6 B$ / $\mathrm{m^3 mol^{-1}}$	$10^{27}\,{}_{\mathrm{m}}C$ / $\mathrm{m^5 A^{-2} mol^{-1}}$
449.9	9	302	-44	-1.060 ± 0.023
439.4	8	301	-46	-0.962 ± 0.025
412.4	10	389	-55	-1.131 ± 0.027
409.5	9	392	-56	-1.151 ± 0.026
378.0	8	300	-70	-1.208 ± 0.021
370.0	9	500	-74	-1.199 ± 0.014
358.2	11	493	-81	-1.358 ± 0.028
348.8	7	399	-86	-1.326 ± 0.013
339.4	10	798	-93	-1.283 ± 0.025
329.9	7	350	-99	-1.399 ± 0.010
317.1	11	800	-109	-1.426 ± 0.020
296.7	11	913	-125	-1.543 ± 0.015
295.2	5	780	-127	-1.562 ± 0.010
293.7	5	550	-128	-1.572 ± 0.010

TABLE 6.2 COTTON-MOUTON EFFECT OF CARBONYL SULFIDE AT λ = 632.8 nm (a)

T / K	No. of pressures	Maximum p / kPa	$10^{27}{}_{\mathrm{m}}C$ / $\mathrm{m^5A^{-2}mol^{-1}}$
464.1	6	125	-2.874 ± 0.021
457.9	10	197	-2.824 ± 0.045
435.5	6	115	-3.122 ± 0.072
398.7	5	250	-3.330 ± 0.035
388.8	5	135	-3.367 ± 0.043
381.4	8	300	-3.577 ± 0.035
360.0	8	300	-3.721 ± 0.019
340.0	8	299	-3.932 ± 0.020
318.7	9	198	-4.189 ± 0.025
318.1	5	299	-4.295 ± 0.036
303.5	8	199	-4.347 ± 0.050
298.0	10	199	-4.474 ± 0.037

(a) Gas densities calculated using van der Waals constants, $a = 0.398$ Pa $\mathrm{m^6\ mol^{-2}}$ and $b = 5.82 \times 10^{-5}\,\mathrm{m^3mol^{-1}}$, reference 3.

TABLE 6.3 COTTON-MOUTON EFFECT OF CARBON DISULFIDE AT $\lambda = 632.8$ nm

T / K	No. of pressures	Maximum p / kPa	$10^6 B$ / $\mathrm{m^3 mol^{-1}}$	$10^{27}{}_{\mathrm{m}}C$ / $\mathrm{m^5 A^{-2} mol^{-1}}$
489.7	11	168	-273	-11.91 ± 0.19
470.8	6	125	-306	-12.17 ± 0.29
449.0	13	160	-344	-13.00 ± 0.14
422.5	13	180	-390	-14.10 ± 0.19
406.4	10	135	-418	-14.75 ± 0.30
385.2	15	175	-465	-15.29 ± 0.10
365.3	12	148	-519	-16.39 ± 0.16
347.3	14	135	-577	-17.00 ± 0.09
336.1	16	130	-622	-17.65 ± 0.18
321.5	9	32	-682	-18.37 ± 0.27
311.1	15	32	-744	-19.23 ± 0.16
303.3	9	32	-772	-19.65 ± 0.29
292.7	12	32	-845	-20.69 ± 0.35

in which the terms have their usual meanings. As previously discussed, the classical equation can be modified to account for contributions from rotation-induced magnetic moments, as in equation (1.9):

$$A_{\mathrm{C}} = \frac{N_{\mathrm{A}}\mu_0^2}{270\varepsilon_0}\left[\left(\eta_{\alpha\beta:\alpha\beta} - \frac{1}{3}\eta_{\alpha\alpha:\beta\beta}\right) + \frac{2\Delta\alpha\Delta\chi}{3kT}\left(1 - \sigma_0 + \frac{8}{15}\sigma_0^2 - \ldots\right)\right] \qquad (6.2)$$

where $\sigma_0 = \frac{hcB_0}{kT}$ and B_0 is the rotational constant in the ground vibrational state. The correction factor for carbon dioxide is taken to the second term, and amounts to at most 0.5%; for carbonyl sulfide and carbon disulfide, the factors were negligible.

The linear dependence of ${}_{\mathrm{m}}C$ on T^{-1} predicted by this equation was observed in each case and is shown in Figures 6.1, 6.2 and 6.3; the results of a weighted least-squares fitting procedure are given in Tables 6.4, 6.5 and 6.6, where results from a study by Kling and Hüttner, and by others where appropriate, are shown for comparison.

The temperature-independent contributions to the Cotton-Mouton constants at 298 K are -3 ± 5%, -1 ± 2% and -4 ± 1%, respectively, for carbon dioxide, carbonyl sulfide and carbon disulfide. Despite the somewhat uncertain extrapolation to $T^{-1} = 0$, it can be concluded that in each case the magnetic hyperpolarizability term is a small contributor in the presence of the much larger orientational term. Despite the large uncertainties, the present values of the magnetic hyperpolarizability anisotropy, with the exception of that for carbon dioxide, are in disagreement with those determined in the previous study,[1] and no explanation can be offered for this discrepancy. Unfortunately, ab initio calculations of this property have not yet been extended to species of such complexity.

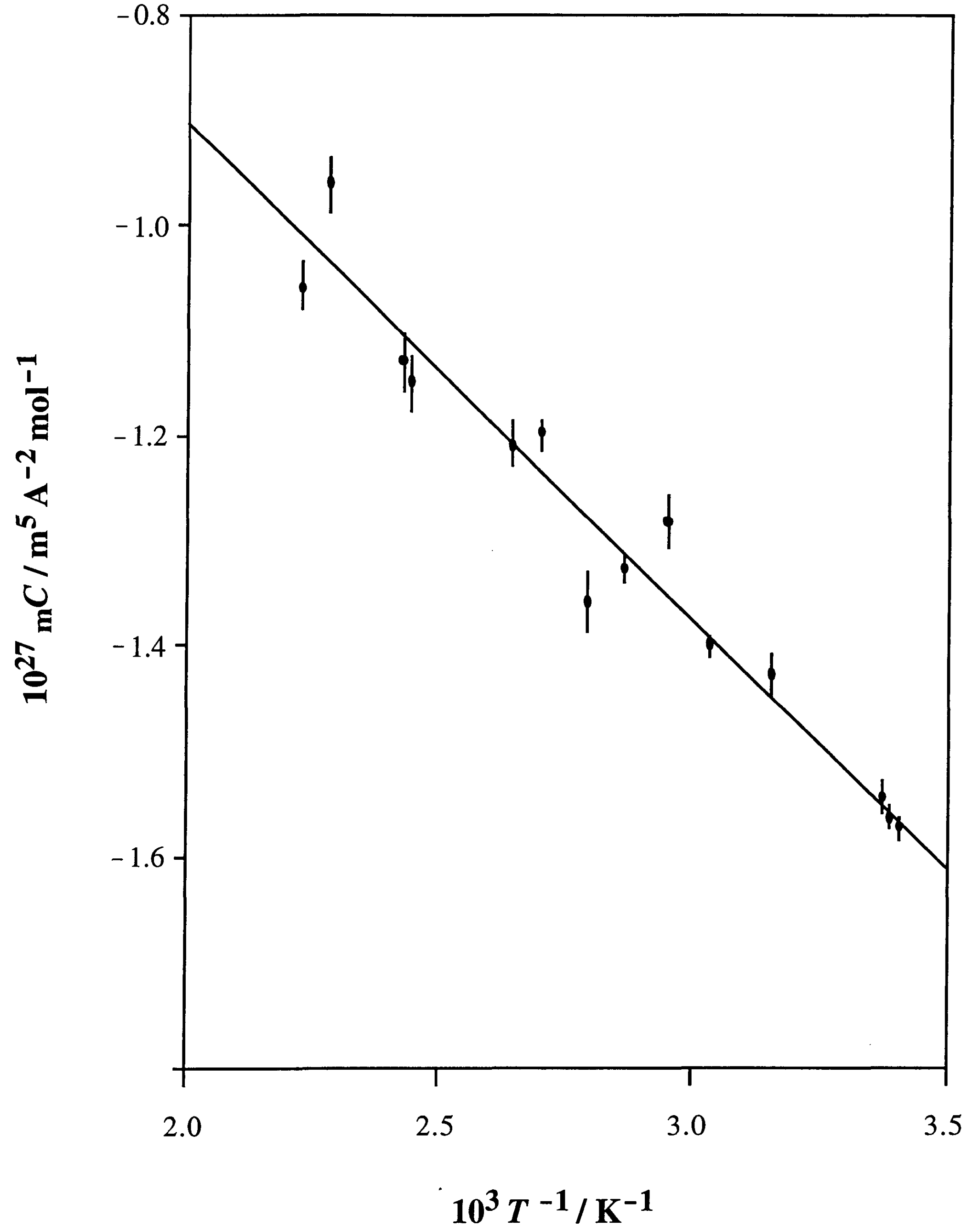

Figure 6.1 Temperature dependence of the Cotton-Mouton effect of carbon dioxide.

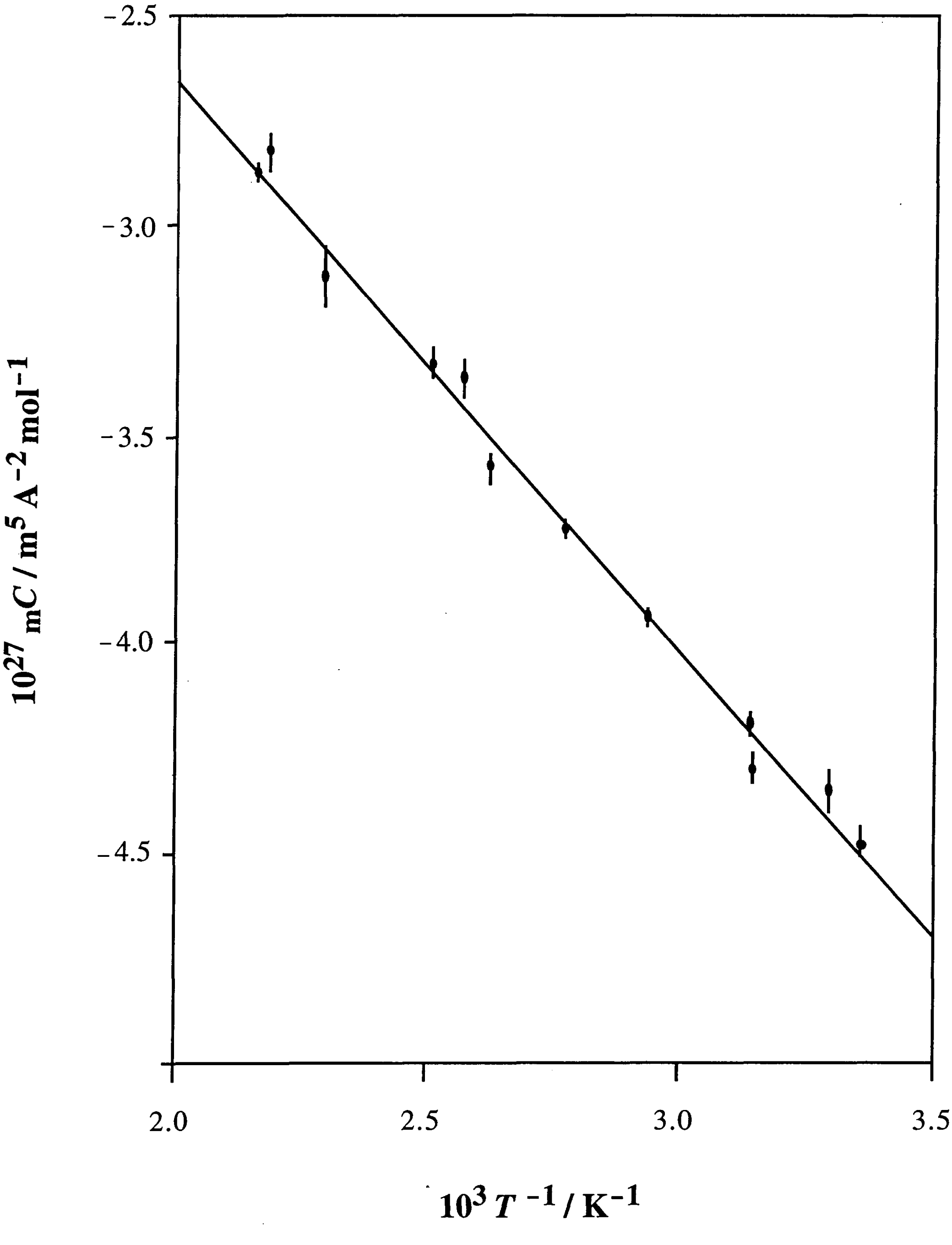

Figure 6.2 Temperature dependence of the Cotton-Mouton effect of carbonyl sulfide.

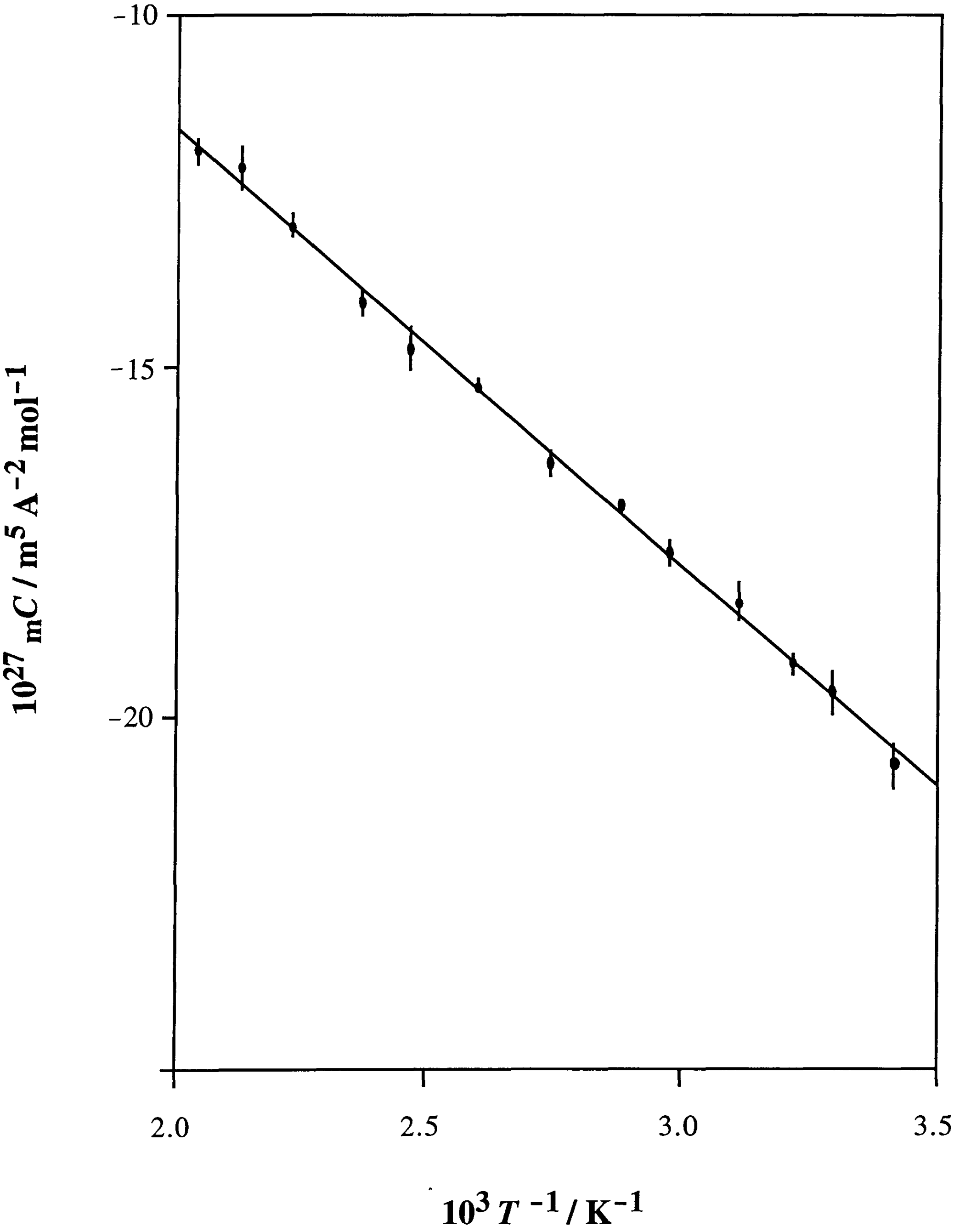

Figure 6.3 Temperature dependence of the vapour-state Cotton-Mouton effect of carbon disulfide.

TABLE 6.4 ANALYSIS OF THE TEMPERATURE DEPENDENCE OF THE COTTON-MOUTON EFFECT OF CARBON DIOXIDE AT $\lambda = 632.8$ nm

Property	Value	Literature value
10^{27}intercept / $m^5A^{-2}mol^{-1}$	0.040 ± 0.066	
10^{24}slope / $m^5A^{-2}K\,mol^{-1}$	-0.472 ± 0.022	
$10^{50}\Delta\eta$ / $C\,m^2V^{-1}T^{-2}$	10 ± 17	-16 ± 10 (a)
$10^{68}\Delta\alpha\Delta\chi$ / $C^2m^2T^{-4}$	-2.46 ± 0.11	-2.46 ± 0.04 (a)
$10^{40}\Delta\alpha$ / $C\,m^2V^{-1}$ (b)	2.35 ± 0.07	
$10^{29}\Delta\chi$ / $J\,T^{-2}$	-10.46 ± 0.58	-10.48 ± 0.36 (a)
g (c)	-0.05508 ± 0.00005	
B_0 / GHz (d)	11.698	
$10^{40}\Theta$ / $C\,m^2$	-14.1 ± 1.2	-14.0 ± 0.8 (a)

(a) Reference 1.

(b) Reference 4.

(c) Reference 5.

(d) Reference 6.

TABLE 6.5 ANALYSIS OF THE TEMPERATURE DEPENDENCE OF THE COTTON-MOUTON EFFECT OF CARBONYL SULFIDE AT $\lambda = 632.8$ nm

Property	Value	Literature value
10^{27}intercept / $m^5A^{-2}mol^{-1}$	0.061 ± 0.089	
10^{24}slope / $m^5A^{-2}K\,mol^{-1}$	-1.358 ± 0.032	
$10^{50}\Delta\eta$ / $C\,m^2V^{-1}T^{-2}$	15 ± 22	-130 ± 20 (a)
$10^{68}\Delta\alpha\Delta\chi$ / $C^2m^2T^{-4}$	-7.07 ± 0.17	-7.04 ± 0.14 (a)
$10^{40}\Delta\alpha$ / $C\,m^2V^{-1}$ (b)	4.53 ± 0.08	
$10^{29}\Delta\chi$ / $J\,T^{-2}$	-15.61 ± 0.46	-15.54 ± 0.41 (c) -15.55 ± 0.03 (d) -15.56 ± 0.02 (e) -15.39 ± 0.17 (f)
g (e)	-0.028839 ± 0.000006	
B_0 / GHz (g)	6.08149	
$10^{40}\Theta$ / $C\,m^2$	-2.76 ± 0.26	-2.58 ± 0.08 (d) -2.62 ± 0.05 (e) -3.58 (h) -4.5 ± 2.0 (i)

Table 6.5 continues on next page

$10^{30}\mu$ / C m (*j*)	2.38564 ± 0.00003	
Z / Å	0.32 ± 0.14	1.2 (*k*)
$10^{50}\left(2a_1 + a_2 + 3a_3 + \frac{10}{\omega}G'\right)$ / C m^{3}V^{-1}	-2.9 ± 1.3	-14 (*k*)

(*a*) Reference 1.

(*b*) Reference 4.

(*c*) Calculated using $\Delta\alpha$ value (from reference 4) with $\Delta\alpha\Delta\chi$.

(*d*) Microwave Zeeman spectroscopy using superconducting magnet, reference 7.

(*e*) Molecular beam electric resonance Zeeman spectroscopy, reference 8.

(*f*) Conventional microwave Zeeman spectroscopy, reference 9.

(*g*) Reference 10.

(*h*) SCF-CI calculations, reference 11.

(*i*) MCSCF calculations, reference 12.

(*j*) Reference 13.

(*k*) Electric field-gradient induced birefringence, reference 14.

TABLE 6.6 ANALYSIS OF THE TEMPERATURE DEPENDENCE OF THE COTTON-MOUTON EFFECT OF CARBON DISULFIDE AT $\lambda = 632.8$ nm

Property	Value	Literature value
10^{27}intercept / $\mathrm{m^5A^{-2}mol^{-1}}$	0.78 ± 0.26	
10^{24}slope / $\mathrm{m^5A^{-2}K\,mol^{-1}}$	-6.20 ± 0.10	
$10^{50}\Delta\eta$ / $\mathrm{C\,m^2V^{-1}T^{-2}}$	200 ± 70	-260 ± 160 (*a*)
$10^{68}\Delta\alpha\Delta\chi$ / $\mathrm{C^2m^2T^{-4}}$	-32.3 ± 0.5	-32.4 ± 1.2 (*a*)
$10^{40}\Delta\alpha$ / $\mathrm{C\,m^2V^{-1}}$ (*b*)	10.53 ± 0.21	
$10^{29}\Delta\chi$ / $\mathrm{J\,T^{-2}}$	-30.7 ± 0.8	-30.7 ± 2.0 (*a*)
g (*c*)	-0.02274 ± 0.00002	
B_0 / GHz (*d*)	3.2713 ± 0.0002	
$10^{40}\Theta$ / $\mathrm{C\,m^2}$	13.9 ± 1.8	13.9 ± 4.5 (*a*)

(*a*) Reference 1.

(*b*) Reference 4.

(*c*) Reference 5.

(*d*) Reference 15.

Reliable values for the polarizability anisotropies, obtained from measurements of Rayleigh depolarization ratios,[4] were used to evaluate the magnetic anisotropy, $\Delta\chi$, for each of these molecules. It is immediately apparent that the present values of $\Delta\chi$ are in good agreement with those in the previous study, despite the differences in the temperature-independent magnetic hyperpolarizability anisotropies. Furthermore, for carbonyl sulfide, there is excellent agreement with values obtained directly from microwave Zeeman effect studies, as shown in Table 6.5.

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

$$\Theta = \frac{eIg}{m_p} - \left(\frac{4m_e}{e}\right)\Delta\chi \tag{6.3}$$

in which I is the moment of inertia and g is the rotational g value. The quadrupole moment was derived from equation (6.3) using the rotational constant, B_0, from which I can be determined, the rotational g value from molecular beam magnetic resonance spectroscopy and the magnetic anisotropy. Comparisons of the derived values of the quadrupole moments of carbon dioxide and carbon disulfide with previous experimental and theoretical values are shown in Tables 6.7 and 6.8, respectively. The present values are, within experimental errors, in good agreement with those determined from recent measurements of the temperature dependence of electric field-gradient induced birefringence in the gases,[16] although, for obvious reasons, the precision is not as high. Carbon dioxide has been extensively studied and values of its quadrupole moment have been determined through direct and indirect methods. It is of interest to note that values derived from early studies such as collision-induced microwave absorption and use of pressure second virial coefficients allowed the magnitude of the quadrupole moment to be determined. More recent experimental

TABLE 6.7 VALUES OF THE MOLECULAR QUADRUPOLE MOMENT OF CARBON DIOXIDE

Year	Method	$10^{40}\Theta$ / C m^2	Ref.
	Experiment		
1957	Collision-induced microwave absorption	±11.4 ± 0.9	17
1959	Pressure second virial coefficients and crystal data	±15.3	18
1962	Collision-induced microwave absorption	±19.7	19
1963	Single-temperature electric field-gradient induced birefringence	-13.7 ± 0.7	20
1964	Collision-induced microwave absorption	±14.4	21
1965	Nuclear spin relaxation	±16.2	22
1968	Single-temperature electric field-gradient induced birefringence	-14.3 ± 0.8	14
1970	Dielectric and pressure second virial coefficients	±14.3, ±13.7	23
1970	Collision-induced far-infrared absorption	±21.3, ±25.4	24
1971	Collision-induced far-infrared absorption	±14.9 ± 0.7	25
1977	Ion-molecule scattering	±14.7 ± 3.3	26
1981	Temperature dependence of electric field-gradient induced birefringence	-15.0 ± 0.5	27

Table 6.7 continues on next page

1984	Experimental value of $\Delta\chi$ (Cotton-Mouton effect) and g value	-14.0 ± 0.8	1
1989	Single-temperature electric field-gradient induced birefringence	-13.4 ± 0.7	28
1994	Temperature dependence of electric field-gradient induced birefringence	-14.3 ± 0.6	16
1994	Experimental value of $\Delta\chi$ (Cotton-Mouton effect) and g value (this work)	-13.7 ± 1.3	
	Theory		
1963	SCF calculations	-8.3	29
1973	SCF calculations	-17.5	30
1976	MCSCF/CI calculations	-19.7	31
1978	MCSCF calculations	-15.2	12
1985	SCF calculations	-12.5	32
1985	MP2 calculations	-12.3	33
1989	MP2 calculations	-13.3	34
1989	MP4 calculations	-14.1	35
1989	SDQ-MP4 calculations	-14.7	35
1990	SDQ-MP4 calculations	-14.5	36
1994	Semi-empirical PM3/NAO-PC calculations	-20.9	37

TABLE 6.8 VALUES OF THE MOLECULAR QUADRUPOLE MOMENT OF CARBON DISULFIDE

Year	Method	$10^{40}\Theta$ / C m^2	Ref.
	Experiment		
1956	Collision-induced microwave absorption	±5.9	38
1970	Viscosity and density second virial coefficients	±22.7	39
1980	Solution-phase electric birefringence	14.2 ± 1.1	40
1981	Single temperature electric field-gradient induced birefringence	12.0 ± 0.6	27
1984	Experimental value of $\Delta\chi$ (Cotton-Mouton effect) and g value	13.9 ± 4.5	1
1994	Temperature dependence electric field-gradient induced birefringence	11.5 ± 0.5	16
1994	Experimental value of $\Delta\chi$ (Cotton-Mouton effect) and g value (this study)	13.9 ± 1.8	
	Theory		
1978	MCSCF calculations	7.0 ± 3.0	12
1979	SCF calculations	11.1	41
1985	SCF calculations	11.1	32
1989	MP2 calculations	11.8	34
1992	SCF calculations	10.9	42

studies and theoretical calculations have established the magnitude and the sign of the quadrupole moment. Clearly, the quality of the basis sets and the methods used in theoretical studies have improved and the agreement between the more recent experimental and theoretical values is now excellent. The most recent theoretical value is in poor agreement with other values and this can be attributed to its point charge model which does not sufficiently account for the charge distribution within the molecule. For carbon disulfide, relatively few measurements of the quadrupole moment have been reported, with the most reliable values derived from vapour- and solution-phase measurements of the electric field-gradient induced birefringence effect. Recent theoretical values also support the present value within its experimental uncertainty. From interpolation of Rayleigh depolarization ratios determined by Alms, *et al*,[43] a value of $\Delta\alpha$ higher by approximately 3% is obtained, compared with that used in the present analysis, from which $\Delta\chi = -29.9\times10^{-29}\,\mathrm{J\,T^{-2}}$ and $\Theta = 12.1\times10^{-40}\,\mathrm{C\,m^2}$.

For dipolar molecules, such as carbonyl sulfide, the quadrupole moment is origin-dependent. The molar field-gradient birefringence constant, ${}_{\mathrm{m}}Q$, determined from electric field-gradient induced birefringence studies, can be related to fundamental molecular properties, for a linear species, by the equation[44,45]

$${}_{\mathrm{m}}Q = \frac{2N_{\mathrm{A}}}{45\varepsilon_0}\left\{\frac{15}{2}B + \frac{1}{kT}\left[\Theta\Delta\alpha - \frac{1}{2}\mu\left(2a_1 + a_2 + 3a_3 + \frac{10}{\omega}G'\right)\right]\right\} \qquad (6.4)$$

where B is, in this instance, the quadrupole hyperpolarizability; μ is the permanent molecular dipole moment; ω is the frequency of the incident radiation; a_1, a_2 and a_3 are related to the dipole-quadrupole polarizability tensor, A, and G' is the optical activity tensor; the latter two being fundamental properties describing asymmetry in the distribution of the molecular polarizability.[46] In the above expression, the origin of the quadrupole moment is the effective quadrupole centre, whereas the Zeeman effect yields the moment relative to the centre of mass. The effective quadrupole centre can be considered as the point at which the first moment of the polarizability anisotropy vanishes.[14] If the centre of mass is a distance Z from the effective quadrupole centre in the direction of the dipole moment, then the centre-of-mass quadrupole moment, Θ_{CM}, is related to the effective quadrupole moment, Θ_{EQC}, by the expression[14]

$$\Theta_{\mathrm{CM}} - \Theta_{\mathrm{EQC}} = -2\mu Z \qquad (6.5)$$

from which a value of Z can be determined if Θ_{CM} and Θ_{EQC} are known. In addition, the combination of Z and $\Delta\alpha$ provides a route to information concerning the higher polarizabilities, a and G', from the relation[14]

$$\left(2a_1 + a_2 + 3a_3 + \frac{10}{\omega}G'\right) = -2\Delta\alpha Z \qquad (6.6)$$

The analysis of the experimental results for carbonyl sulfide is shown in Table 6.5, which includes a comparison of values of the quadrupole moment from the literature. Results from the study of the electric field-gradient induced birefringence[14] were reanalyzed using revised values for $\Delta\chi$, g, μ and $\Delta\alpha$, and values for Z and the combination of the higher polarizabilities, a and G', are also shown in Table 6.5. Other values of the above combination of a and G' have been published, but such data are limited.[47] Theoretical calculations of the necessary components of the tensors are available only for relatively simple species,[48] and there is scope for further work in this area.

This study has shown that, at room temperature, the temperature-independent contributions to the Cotton-Mouton constants in these strongly anisotropic molecules are very much smaller than the orientational contributions, and can be considered negligible. More importantly, the comparison of results from this and the previous study is very favourable, although the disagreement with the magnetic hyperpolarizability anisotropy values is of some concern. The agreement of values of the magnetic anisotropy and quadrupole moment, obtained from a range of independent techniques, is acceptable and further enhances confidence in the procedure used here. For carbonyl sulfide, a combination of elements of the dipole-quadrupole polarizability and the optical activity tensor was evaluated. While it is obviously desirable to determine the quadrupole moment of a non-polar molecule from measurements of the temperature dependence of electric field-gradient induced birefringence, the indirect method using the magnetic anisotropy and the g value can be used to obtain accurate values of Θ, as shown in the present study.

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