CHAPTER 7 - TEMPERATURE DEPENDENCE OF THE COTTON-MOUTON EFFECT OF ETHANE

7.1 INTRODUCTION

Reliable measurements of the polarizability anisotropy and other fundamental electric and magnetic properties of small molecules such as cyclopropane,[1] cyclohexane,[2] acetylene[3] and ethane[4,5] are of interest. In addition to their intrinsic value, there are now reliable ab initio methods for computing these properties, and therefore measurements of the properties are important to test theoretical predictions. Furthermore, attempts to describe the behaviour of saturated hydrocarbons in terms of bond properties derived from methane and ethane have been and remain a useful first approximation. Such behaviour includes intermolecular forces and the intensity of Raman scattering,[6] and the properties of ethane, the simplest saturated hydrocarbon with a carbon-carbon bond, are often pivotal in such schemes. The determination of the molecular polarizability anisotropy of ethane has been the subject of many investigations employing a wide variety of experimental and theoretical techniques. Recently, the polarizability anisotropies of a number of small molecules, including ethane, have been analyzed to determine isotropic and anisotropic dispersion interaction energy coefficients,[7] and this further highlights the need for reliable experimental values of the molecular properties.

Considering the relative importance of the polarizability anisotropy for ethane, it is surprising that there is considerable uncertainty regarding its magnitude: reported values[4,8-13] of $\Delta\alpha$ vary from 0.61×10^{-40} to 0.82×10^{-40} C m^{2}V^{-1}. The Rayleigh depolarization ratio of a gas offers the most direct route to the determination of the polarizability anisotropy; but it is well recognized[12-15] that if the molecule is only

weakly anisotropic, as is the case with ethane, the depolarization ratio obtained by conventional methods[10] is likely to be an overestimate unless spurious contributions from depolarized vibrational Raman scattering are excluded. Studies[12,13] which excluded these contributions yielded much lower and presumably more reliable values, and the issue appeared resolved. More recently, however, two independent techniques[5,16] were used to determine the polarizability anisotropy of ethane, and the values were significantly higher than those obtained from the supposedly improved Rayleigh scattering studies. A microwave Zeeman effect study[5] of CH_3CD_3 provided a value for the magnetic anisotropy, which was used in the analysis of the previous Cotton-Mouton effect data[4] for CH_3CH_3 to determine the optical-frequency polarizability anisotropy of ethane; and a Stark effect study[16] of CH_3CD_3 provided a value of the static polarizability anisotropy which, when dispersion was taken into account, supported the value obtained from the former method.

To resolve the discrepancy, a study of the temperature dependence of the Cotton-Mouton effect of ethane was conducted and this, in combination with a recent study of the temperature dependence of the electric field-gradient induced birefringence,[17] and the known g values and moments of inertia, yielded reliable values of the magnetic anisotropy, the polarizability anisotropy and the quadrupole moment. Unlike the work of Hüttner, *et al*,[5] the use of values derived from isotopic species was avoided in the present work. In addition, the study of the temperature dependence of the Kerr effect of ethane was repeated,[18] and the derived polarizability anisotropy was used to determine the static polarizability anisotropy. Using infrared band intensities to estimate the vibrational contribution and from the data for the dispersion of the Rayleigh depolarization ratio for the electronic contribution, an alternative value of the static polarizability anisotropy was obtained, and compared with those obtained from the present work and the Stark effect study.

7.2 EXPERIMENTAL RESULTS

The sample of ethane (Matheson, research grade), used without further purification, was analyzed by gas chromatography to confirm the purity as $> 99.96\%$. Measurements of the birefringence at $\lambda = 632.8$ nm were made at 18 temperatures spanning of the range 280-400 K, and, at each temperature, over a range of pressure (up to 900 kPa). Below ambient temperature, measurements were achieved using various cooling mixtures, typically ice-water-salt, in a specially constructed bath which surrounded the cell. Gas densities were calculated from measured gas pressures and temperatures using published density second virial coefficients.[19] Results are summarized in Table 7.1, 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[4] which was performed at ≈ 40 temperatures in the range ≈ 200-390 K, a span of ≈ 190 K rather than 120 K, and at pressures up to ≈ 100 kPa; the two sets of results are compared in the next section.

7.3 ANALYSIS AND DISCUSSION

For molecules with an axis of threefold or higher symmetry, the equation describing the temperature dependence of $_mC$ is:

$$_mC = \frac{N_A\mu_0^2}{270\varepsilon_0}\left(\Delta\eta + \frac{2\Delta\alpha\Delta\chi}{3kT}\right)$$ (7.1)

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

TABLE 7.1   COTTON-MOUTON EFFECT OF ETHANE AT $\lambda = 632.8$ nm

T / K	No. of pressures	Maximum p / kPa	$10^6 B$ / $m^3 mol^{-1}$	$10^{27}{}_m C$ / $m^5 A^{-2} mol^{-1}$
401.1	13	300	−95	−0.300 ± 0.015
400.3	10	398	−96	−0.280 ± 0.015
397.0	9	350	−98	−0.267 ± 0.024
378.3	13	496	−109	−0.315 ± 0.014
355.7	10	497	−125	−0.339 ± 0.014
354.2	8	400	−127	−0.342 ± 0.015
339.2	15	448	−140	−0.357 ± 0.014
335.1	7	495	−144	−0.375 ± 0.017
334.0	9	506	−145	−0.351 ± 0.012
321.3	7	696	−158	−0.367 ± 0.014
319.2	8	698	−160	−0.387 ± 0.008
304.0	12	906	−177	−0.382 ± 0.007

297.9	8	698	-180	-0.388 ± 0.011
296.9	7	500	-187	-0.380 ± 0.025
295.8	14	708	-188	-0.396 ± 0.005
285.0	9	700	-204	-0.421 ± 0.014
283.2	9	802	-207	-0.447 ± 0.011
281.1	10	300	-210	-0.424 ± 0.037

Figure 7.1. If the line is extrapolated to $T^{-1} = 0$, the intercept determines $\Delta\eta$ and the slope $\Delta\alpha\Delta\chi$. The results of a weighted least-squares fitting procedure and subsequent analysis, in terms of the relevant molecular properties, are summarized in Table 7.2, where results from the previous study[1] are shown for comparison.

Further comparison is detailed in Figure 7.2: line A (present measurements) is the weighted-fit least-squares straight line derived from the results in Table 7.1 (with the actual points shown without uncertainties for clarity); 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 (281-391 K) that is common to the two investigations, the absolute values of the small Cotton-Mouton constant of ethane differ by less than 10%; however, the actual data sets and the somewhat long extrapolations to $T^{-1} = 0$ produce seriously discordant values of the intercepts and slopes and, as shown in Table 7.2, the derived molecular properties. Clearly, the comparison made here is similar to that for acetylene, detailed in an earlier chapter.

It is immediately obvious that the value of $\Delta\eta$ (expressed as $10^{50}\Delta\eta$ / $C\,m^2V^{-1}T^{-2}$) and the percentage contribution that it makes to the Cotton-Mouton constant at 298 K (2 ± 8, $-2 \pm 8\%$) are very much smaller than indicated by the earlier measurements (25 ± 5, $-24 \pm 5\%$). Nevertheless, there are no qualitative grounds for a choice between these results, as such values are often poorly determined by experiments of this kind and, as mentioned previously, ab initio computations of this property have not yet been extended to species of this complexity.

On treating ethane as a rigid species, the microwave Zeeman effect study[5] of CH_3CD_3 provided, directly, a value of the magnetic anisotropy which was combined with the value of $\Delta\alpha\Delta\chi$ determined in the previous Cotton-Mouton effect study[4] to evaluate $\Delta\alpha$. In the present work, $\Delta\alpha\Delta\chi$ was analyzed in conjunction with the value
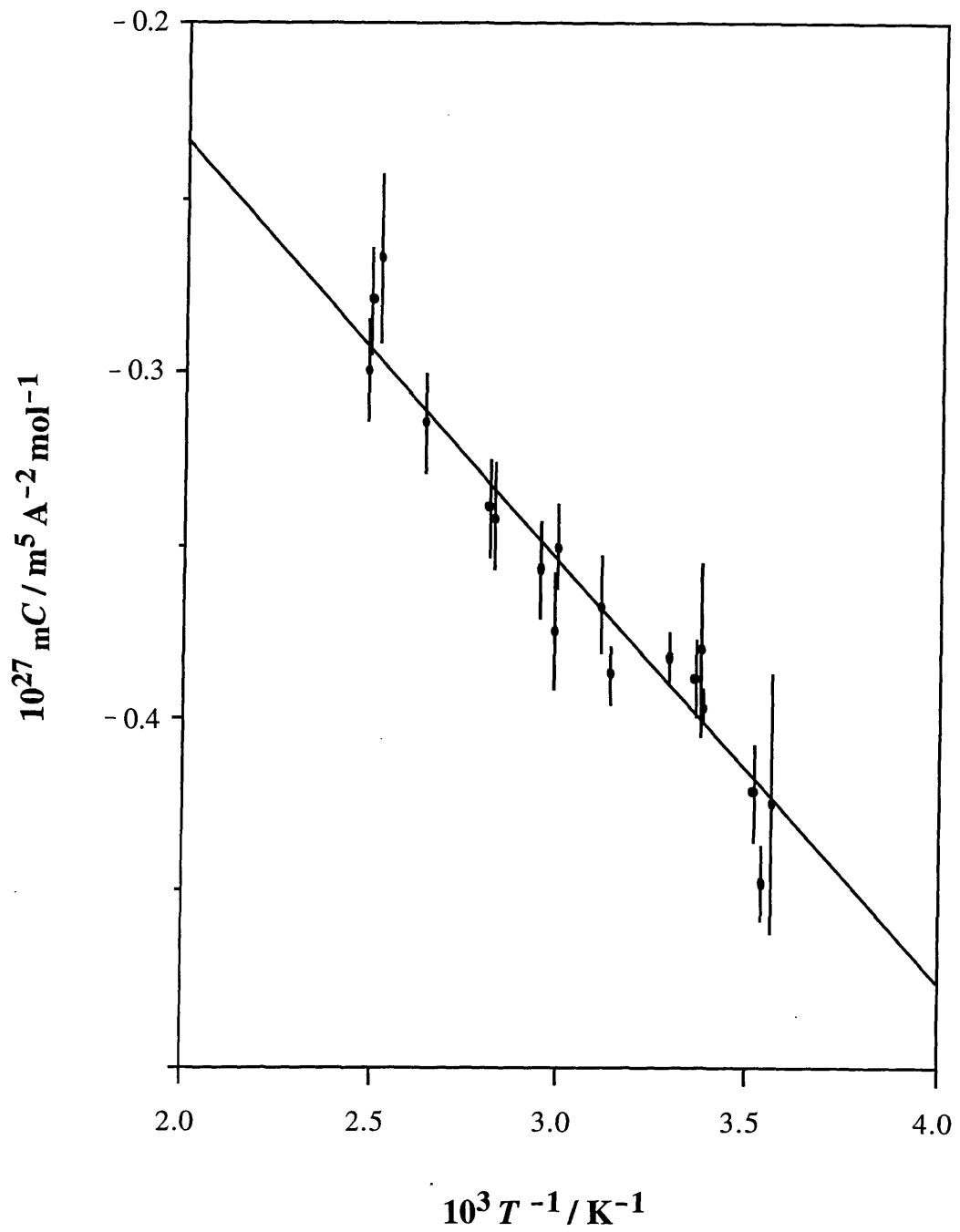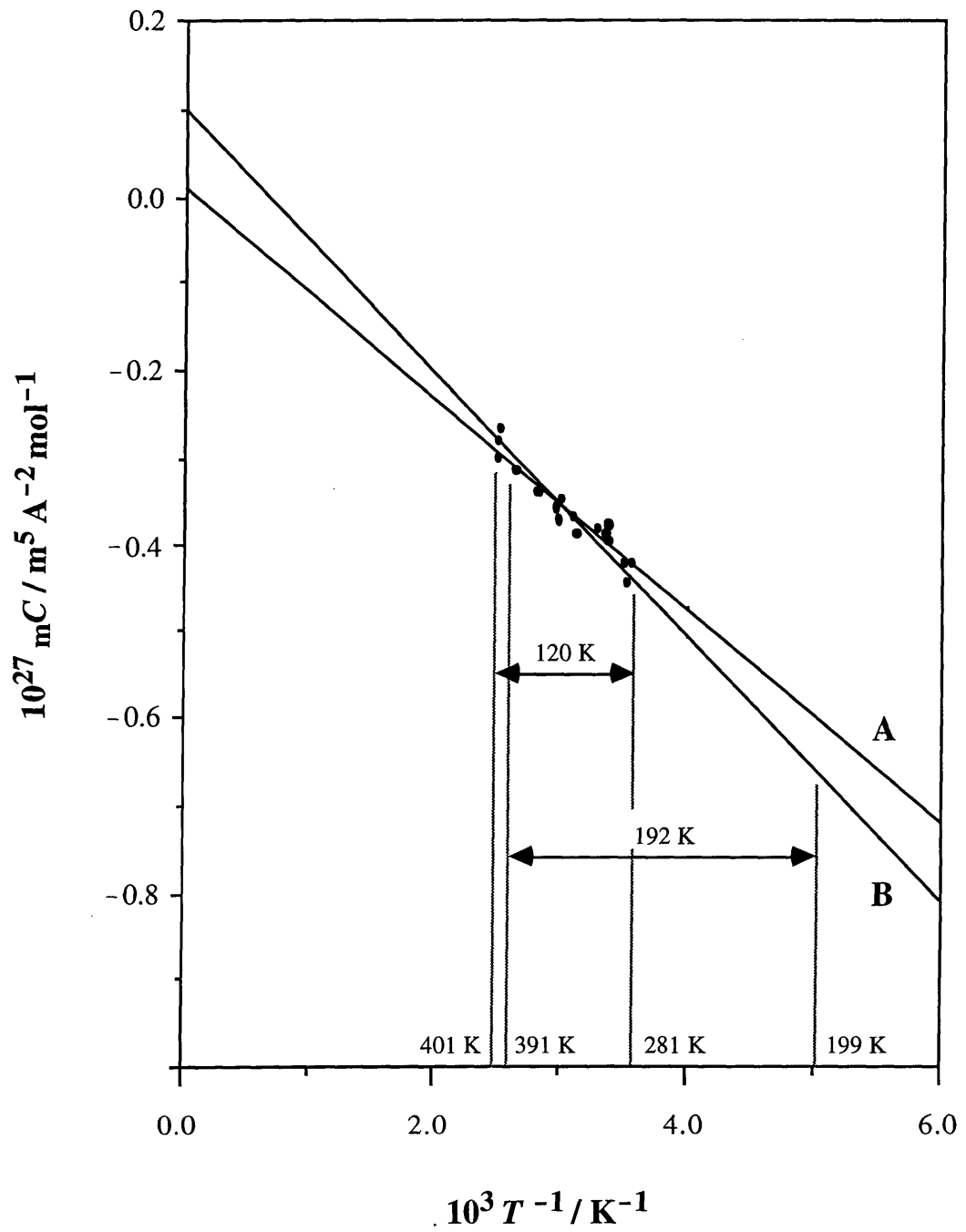
<u>Figure 7.1</u>   Temperature dependence of the Cotton-Mouton effect of ethane.

Figure 7.2   Comparison of the temperature dependences of the Cotton-Mouton effect of ethane.

Line A, present study, with actual data points shown; line B, reference 4, without actual data points shown.

TABLE 7.2   ANALYSIS OF THE TEMPERATURE DEPENDENCE OF THE COTTON-MOUTON EFFECT OF ETHANE AT $\lambda = 632.8$ nm

Property	Value	Literature value
10^{27} intercept / $m^5 A^{-2} mol^{-1}$	0.008 ± 0.032	
10^{24} slope / $m^5 A^{-2} K\, mol^{-1}$	-0.121 ± 0.010	
$10^{50} \Delta\eta$ / $C\, m^2 V^{-1} T^{-2}$	2 ± 8	25 ± 5 [a]
$10^{69} \Delta\alpha\Delta\chi$ / $C^2 m^2 T^{-4}$	-6.30 ± 0.52	-7.93 ± 0.29 [a]
$10^{80} \Theta\Delta\alpha$ / $C\, m^2 V^{-1}$ [b]	-1.75 ± 0.12	
g_{zz} [c]	0.2468 ± 0.0004	
g_{xx} [c]	0.00402 ± 0.00020	
$10^{47} I_{zz}$ / $kg\, m^2$ [d]	10.44	
$10^{47} I_{xx}$ / $kg\, m^2$ [d]	42.27	
$10^{40} \Delta\alpha$ / $C\, m^2 V^{-1}$	0.698 ± 0.056	0.816 ± 0.086 [e]
$10^{29} \Delta\chi$ / $J\, T^{-2}$	-9.04 ± 0.11	-10.03 ± 0.37 [a] -9.73 ± 0.68 [e]
$10^{40} \Theta$ / $C\, m^2$	-2.50 ± 0.26	-2.25 ± 0.15 [b]
$10^{80} \Delta\alpha\Delta\alpha^0$ / $C^2 m^4 V^{-2}$	0.422 ± 0.060 [f]	0.425 ± 0.061 [g]
$10^{40} \Delta\alpha^0$ / $C\, m^2 V^{-1}$	$0.60_5 \pm 0.10$	0.748 ± 0.030 [h]

[a] Reference 4.   [b] Reference 17.   [c] References 5 and 20.

[d] Reference 21.   [e] Reference 5.   [f] Reference 18.

[g] Reference 22.   [h] Reference 16.

of $\Theta\Delta\alpha$, derived from a recent study of the temperature dependence of the electric field-gradient induced birefringence[17] of ethane. The temperature dependence study was necessary to separate the significant contribution of the hyperpolarizability term from the orientational term. The expression for the molecular quadrupole moment of a rigid, planar, axially symmetric molecule can be obtained through a rearrangement of equation (1.24):

$$\Theta = -\frac{e}{m_p}\left(g_{zz}I_{zz} - g_{xx}I_{xx}\right) - \left(\frac{4m_e}{e}\right)\Delta\chi \qquad (7.2)$$

in which g_{zz}, g_{xx} are the rotational g values and I_{zz}, I_{xx} are the principal moments of inertia parallel and perpendicular to the symmetry axis, respectively. Therefore, the values of the polarizability anisotropy, the quadrupole moment and the magnetic anisotropy can be evaluated when the equations for $\Delta\alpha\Delta\chi$, $\Theta\Delta\alpha$ and Θ are solved simultaneously using reliable g values and moments of inertia. A chronological summary of previous experimental and theoretical values of $\Delta\alpha$ has been prepared as Table 7.3 to facilitate discussion. It is apparent that the values of $\Delta\chi$ obtained here and from the Zeeman effect study are in agreement, and this supports the assumption that the effects of deuteration on the values of $\Delta\chi$ are negligible.[5]

In relation to the optical-frequency polarizability anisotropy, the difference in the slopes of the plots of $_mC$ against T^{-1} (Table 7.2) is such that the value of $\Delta\alpha$ (in units of 10^{-40} $C\,m^2V^{-1}$) determined in this study (0.698 ± 0.056) is significantly smaller than that given by the previous investigation (0.816 ± 0.086). As with the investigation of acetylene, it appears that the low-temperature Cotton-Mouton constants in the earlier study[4] are somewhat unreliable, thus causing a significant error in the determinations of $\Delta\alpha\Delta\chi$ and $\Delta\eta$. It should be noted, however, that there is good agreement between the two groups in the temperature dependence studies of the Cotton-Mouton effects of C_6H_6,[23] O_2,[24] CO_2, OCS and CS_2, all of which are more

TABLE 7.3   VALUES OF THE MOLECULAR POLARIZABILITY ANISOTROPY OF ETHANE

Year	Method	$10^{40}\Delta\alpha$ / $C\,m^2V^{-1}$	Ref.
1966	Rayleigh scattering at λ = 632.8 nm, direct measurement of ρ_0	0.858 ± 0.004	8
1977	Rayleigh scattering at λ = 488.0 nm, direct measurement of ρ_0	0.803 ± 0.028	9
1978	Rayleigh scattering at λ = 488.0, 514.5, and 632.8 nm, direct measurement of ρ_0, 3% ethylene impurity	0.700 ± 0.004	10
1979	Rayleigh scattering at λ = 514.5 and 632.8 nm, direct measurement of ρ_0	0.744 ± 0.033	11
1982	Rayleigh scattering and rotational Raman effect at λ = 488.0 nm	0.614 ± 0.028	12
1983	Rayleigh scattering at λ = 514.5 nm, direct measurement of ρ_0 with filter to exclude vibrational Raman lines	0.670 ± 0.010	13
1984	Temperature dependence of the Cotton-Mouton effect of CH_3CH_3 at λ = 632.8 nm and microwave Zeeman effect of CH_3CD_3	0.816 ± 0.086	5
1994	Temperature dependences of the Cotton-Mouton effect and electric field-gradient induced birefringence, at λ = 632.8 nm	0.698 ± 0.056	

anisotropic than C_2H_6 and C_2H_2. For a molecule such as ethane that is only weakly anisotropic, the value of $\Delta\alpha$ is unusually small, and, therefore, the observed Rayleigh depolarization ratio is likely to be an overestimate, since contributions from depolarized vibrational Raman scattering were not excluded. Methods which excluded Raman scattering contributions yielded values of $\Delta\alpha$ significantly smaller than previously reported and there is excellent agreement between the present value of $\Delta\alpha$ and the values from the improved methods.[12,13] The agreement is not as satisfactory with the lower value[12] determined using a spectroscopic method suggested by Murphy,[14] in which the rotational Raman spectrum is simulated and the total intensity corrected for the portion of the Rayleigh band omitted, and therefore any discrepancy may be attributed to deficiencies in the simulation of the spectrum.

The polarizability anisotropies of alicyclic or aliphatic hydrocarbon molecules with regular tetrahedral bond angles can be expressed in terms of the irreducible bond polarizability tensor, Γ_α, defined as[25]

$$\Gamma_\alpha = \left(\alpha_\parallel^{CC} - \alpha_\perp^{CC}\right) - 2\left(\alpha_\parallel^{CH} - \alpha_\perp^{CH}\right) \tag{7.3}$$

where subscripts $\parallel$ and $\perp$ refer to directions parallel and perpendicular to the axes of the $C-C$ and $C-H$ bonds. With the z-axis coincident with the symmetry axis, it is straightforward to show that for ethane $\Delta\alpha(C_2H_6) = \Gamma_\alpha$ and for cyclohexane $\Delta\alpha(C_6H_{12}) = -2\Gamma_\alpha$. The value of Γ_α (in units of 10^{-40} $C\,m^2V^{-1}$) for ethane is 0.92, whereas the analogous value for cyclohexane, from its Rayleigh depolarization ratio,[15] is 0.70; from Kerr effect measurements of alicyclic hydrocarbons in solution and as pure liquids,[25] the values of Γ_α are taken as 0.79 and 0.89, respectively, and these disparate values indicate the limitations of the bond-additivity model. This approach can be extended to the magnetizability, and the analogous bond magnetizability parameter, Γ_χ, is

$$\Gamma_\chi = \left(\chi_\parallel^{CC} - \chi_\perp^{CC}\right) - 2\left(\chi_\parallel^{CH} - \chi_\perp^{CH}\right) \qquad (7.4)$$

from which it can be shown that $\Delta\chi(C_2H_6) = \Gamma_\chi$ and $\Delta\chi(C_6H_{12}) = -2\,\Gamma_\chi$. The value of Γ_χ (in units of 10^{-29} J T^{-2}) of ethane is -9.0, whereas that deduced for cyclohexane is -9.6,[15] and the fair agreement between these two results provides some support for the bond-additivity approximation in terms of the molecular magnetizability. An analysis by Bothner-By, *et al*,[26] is somewhat inconsistent and was not used here for comparison. Use of a bond-pair approximation[27] provides a better description than a simple bond additivity model, for which the following equation was taken from Hüttner, *et al*,[5]

$$\frac{1}{2}\left(\chi_{\text{methane}} - \chi_{\text{neopentane}}\right) - \chi_{zz\,\text{ethane}} + \chi_{zz\,\text{isobutane}} + \left(\chi_{xx} - \chi_{yy}\right)_{\text{propane}} = 0 \quad (7.5)$$

where χ is the mean magnetizability and the z-axis coincides with the symmetry axis (for propane, the x-axis lies in the plane of the carbon atoms). Using literature values[28] in conjunction with the value of the magnetic anisotropy of ethane determined here, the calculation for the left-hand side of equation (7.5) leads to $(3\pm7)\times10^{-29}$ J T^{-2} which indicates excellent agreement between experiment and theory.

Studies of the temperature dependence of the Kerr effect can provide a route to the determination of $\Delta\alpha$, although not as directly as the Rayleigh scattering techniques. The Kerr effect of ethane was re-examined,[18] and found to be in excellent agreement with previous measurements,[22] and a value for the static polarizability anisotropy was evaluated using the value of $\Delta\alpha$ determined here. The derived value of $\Delta\alpha^0$ is in serious disagreement with that obtained from the molecular-beam laser Stark spectroscopy study[16] of CH_3CD_3. It should be noted that the value of $\Delta\alpha^0$ (in units of 10^{-40} C m^{2}V^{-1}) for CO_2 was revised from 2.89 ± 0.20

(from the Stark effect[29]) to 2.41 ± 0.08 (from the Kerr effect[30]), a decrease of 20% which is similar to the difference for ethane.

In light of this discrepancy, it is useful to estimate $\Delta\alpha^0$ from experimental data by considering the electronic and vibrational contributions separately. The static polarizability anisotropy differs from the optical-frequency value for two reasons: firstly, the dispersion in the electronic component; and secondly, the presence of a contribution from vibrational states of the molecule, which is usually negligible at optical frequencies.

(a) The electronic contribution, $\Delta\alpha^0_{el}$

The dispersion of $\Delta\alpha$ can be interpreted using the following sum-over-states formula:[31]

$$\Delta\alpha_{el} = \alpha_{\parallel} - \alpha_{\perp} = \sum_k \left(\frac{C_{\parallel k}}{\omega^2_{\parallel k} - \omega^2} - \frac{C_{\perp k}}{\omega^2_{\perp k} - \omega^2} \right) \qquad (7.6)$$

where subscripts $\parallel$ and $\perp$ refer to directions parallel and perpendicular to the molecular symmetry (z) axis, C_k are related to the oscillator strengths of the k-th electronic transitions, and ω is the frequency of the incident light. In most cases, one electronic state will be responsible for the bulk of the dispersion in the parallel component, and one for the perpendicular component.[32] If, as is the case in ethane, the principal $\parallel$ and $\perp$ electronic states are close in energy and well removed from optical frequencies, the above equation can be written as

$$\Delta\alpha_{el} \approx \frac{C_{\parallel} - C_{\perp}}{\omega^2_{eff} - \omega^2} \approx \Delta\alpha^0_{el}\left(1 + \frac{\omega^2}{\omega^2_{eff}} + \ldots \right) \qquad (7.7)$$

where ω_{eff} is an effective frequency of the principal transitions and $\Delta\alpha^0_{\text{el}}$ is the electronic contribution to the static polarizability anisotropy. Therefore the anisotropy should show a linear dependence on ω^2, and this behaviour has been observed for a number of small molecules.[10,33] Two Rayleigh scattering studies[10,11] of ethane were used to determine $\Delta\alpha^0_{\text{el}}$ by extrapolation of $\Delta\alpha$ against ω^2 to $\omega^2 = 0$ using least-squares straight lines (Figure 7.3), and the values are shown in Table 7.5. In one study,[10] the depolarization ratios for ethane were recalculated to take into account a 3% ethylene impurity (its depolarization ratio is a factor of ≈ 100 larger than that of ethane) and the revised values of the polarizability anisotropies are significantly smaller.
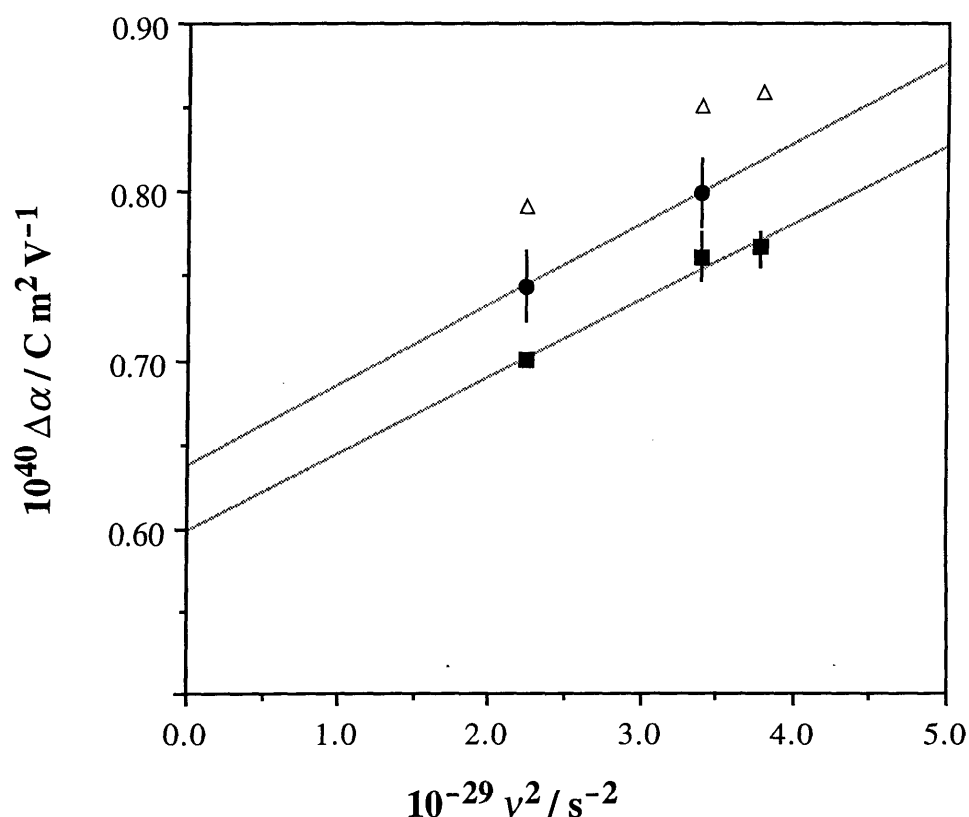
Figure 7.3   Frequency dependence of the polarizability anisotropy of ethane.

△ (without error bars), reference 10; ■, reference 10, recalculated to account for 3% ethylene impurity; ●, reference 11.

Ab initio calculations[34,35] of $\Delta\alpha$ generally yield values for $\Delta\alpha^0_{el}$ and it can be seen from Table 7.5 that there is good agreement between the estimated and theoretical (SCF and MP2) values for ethane. Theoretical calculations have recently been extended to include vibrational motion, and ab initio vibrational averaging studies[36] are in progress with the aim of determining zero-point vibrational corrections for small molecules. Inclusion of zero-point vibrational corrections into electrical properties, such as $\Delta\alpha^0_{el}$, has, in some cases, significantly affected the predicted values of these properties and the agreement with available literature values appears to be very close. A preliminary calculation[36] for ethane has yielded a value of $\Delta\alpha^0_{el} = 0.591 \times 10^{-40} \mathrm{C\,m^2 V^{-1}}$, which is in agreement with those noted above.

(b) The vibrational contribution, $\Delta\alpha^0_{vib}$

Vibrational contributions to the polarizability can be estimated from integrated infrared intensity data, and the vibrational part of $\Delta\alpha^0$ can be determined if the symmetries of the relevant vibrational states are known. The expression for the vibrational contribution to the parallel or perpendicular component of the polarizability is[29]

$$\alpha^0_{vib(\parallel \text{ or } \perp)} / \mathrm{C\,m^2 V^{-1}} = \left(3\varepsilon_0 / 10^6 \pi^2\right) \sum_{j \neq 0} F_j^{-1} g_j^{-1} \sigma_j^{-2} S_j \qquad (7.8)$$

in which g_j is the degeneracy of the vibrational state j, σ_j is the wavenumber (in cm^{-1}) of the transition from the non-degenerate ground state, and S_j is the gas-phase integrated absorption coefficient (in cm molecule^{-1}). The factor F_j is given by:[37]

$$F = B_f I_a Q_v^{-1} \qquad (7.9)$$

where B_f is a Boltzmann factor, $1 - \exp(-E_j/kT)$, which accounts for induced emission, I_a is the isotopic abundance of the main species and Q_v is the vibrational partition function. As the resolution of the infrared spectrum was not sufficient to resolve hot-band intensities, it was appropriate to set the value of Q_v to one; I_a was also assumed to be unity. Using spectroscopic data from the literature,[38] the contributions of individual vibrations are as shown in Table 7.4, and the results of the analysis of the electronic and vibrational polarizability anisotropies are in Table 7.5. Clearly, there is excellent agreement between the estimated values of $\Delta\alpha^0$ and the value derived from the Kerr effect data, and this serves to reinforce the view that the result from the spectroscopic investigation is in error or that the values of $\Delta\alpha^0$ for CH_3CD_3 and CH_3CH_3 are not equivalent.

In summary, the present study has derived reliable values for the optical-frequency and static polarizability anisotropies, the quadrupole moment and the magnetic anisotropy of ethane from an analysis of the temperature dependences of the Cotton-Mouton effect, the Kerr effect and the electric field-gradient induced birefringence studies. In particular, a definitive value of $\Delta\alpha$, not derived from Rayleigh scattering nor estimated from Stark spectroscopy, has confirmed that, for weakly anisotropic species, the depolarization ratio obtained from conventional methods is likely to be too large and methods which remove the spurious contributions from depolarized vibrational Raman scattering must be used. The result for the static polarizability anisotropy has served to emphasize a deficiency, as yet unidentified, in the laser Stark spectroscopic study of this property.

TABLE 7.4   ESTIMATION OF $\Delta\alpha^0_{\text{vib}}$ FROM INFRARED INTENSITY DATA FOR ETHANE

	Symmetry	$\parallel$ or $\perp$	σ_j / cm^{-1}	F^{-1}	$10^{18} S_j$ / cm molec^{-1}	$10^{40}\alpha^0$ / C m^2 V^{-1}
ν_5	a_{2u}	$\parallel$	2954	1.0000	7.938	0.0245
ν_6	a_{2u}	$\parallel$	1379	1.0013	0.664	0.0094
					Total $\alpha^0_{\parallel} =$	0.0339
ν_7	e_u	$\perp$	2996	1.0000	20.046	0.0307
ν_8	e_u	$\perp$	1486	1.0008	2.225	0.0137
ν_9	e_u	$\perp$	820	1.0195	1.013	0.0207
					Total $\alpha^0_{\perp} =$	0.0651

$$\therefore \quad \Delta\alpha^0_{\text{vib}} = \quad -0.031$$

TABLE 7.5   COMPARISON OF EXPERIMENTAL AND ESTIMATED
STATIC POLARIZABILITY ANISOTROPIES OF ETHANE

Anisotropy component	Value
$10^{40} \Delta\alpha^0_{el}$ / C m^2 V^{-1}	0.637,[a] 0.597 [b]
	0.60 (SCF) [c]
	0.551 (SCF), 0.642 (MP2) [d]
$10^{40} \Delta\alpha^0_{vib}$ / C m^2 V^{-1}	-0.031
$10^{40} \Delta\alpha^0_{est}$ / C m^2 V^{-1}	0.606,[a] 0.566 [b]
$10^{40} \Delta\alpha^0_{expt}$ / C m^2 V^{-1}	0.60 ± 0.10 [e]
	0.748 ± 0.030 [f]

[a] Extrapolated using corrected data from reference 10.

[b] Extrapolated using data from reference 11.

[c] Reference 34.

[d] Reference 35.

[e] Present study.

[f] Reference 16.

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CHAPTER 8 - CONCLUSIONS

Improved apparatus[1] has been used to measure the temperature dependence of the Cotton-Mouton effect in various species, and much information about fundamental molecular properties of considerable interest has been obtained and presented in previous chapters of this thesis. The more important conclusions which resulted from this work are briefly summarized in this final chapter.

Previous studies using the original version of this apparatus concentrated on strongly anisotropic species such as benzene and substituted benzenes, and it was considered of great interest to extend the technique to weakly anisotropic species, such as the methyl halides, *etc.* Advantage was taken of computer interfacing, which provided greater signal resolution with longer averaging times and improved ease of data acquisition and analysis. In the present work, difficulties were encountered with some of the measurements. The pressures of species studied were often limited at higher temperatures, due to the bending of the laser beam along the length of the Cotton-Mouton cell. Moreover, the size of the signal decreased as the temperature increased, as expected, and this introduced a greater uncertainty into the results at the higher temperatures. Measurements on weakly anisotropic species, such as ethane, at higher temperatures were very demanding.

Cotton-Mouton second virial coefficients, B_C, were not discernible under the experimental conditions in this work for any of the species studied. Therefore, the assumption that the molar magnetic birefringence constant, $_mC$, is equal to the Cotton-Mouton first virial coefficient, A_C, was valid. Only under high pressures (≈ 200 atm) and low temperatures (≈ 220 K) have contributions from B_C been experimentally observed.[2] At normal temperatures, the orientational term dominated $_mC$ for all the molecules investigated in this project.

Table 8.1 displays the values of the magnetic hyperpolarizability anisotropy and the contributions this term makes to $_mC$ at 300 K for diamagnetic molecules for which reliable data are now available. It can be seen that the magnitude of the magnetic hyperpolarizability anisotropy generally increases as the size of the molecule increases. For the sequence methane-methyl fluoride-methyl chloride-methyl bromide-methyl iodide there seems to be a more or less regular increase in $\Delta\eta$, as was also observed for the series from methane to carbon tetrachloride;[4] however, such simple behaviour does not appear to be exhibited by other molecules studied. The percentage contribution of $\Delta\eta$ to $_mC$ at normal temperatures is relatively small for the highly anisotropic species; but, for weakly anisotropic species, such as oxirane, the contribution can be significant, even large, and certainly cannot be considered negligible. It is of interest that, for most of the anisotropic molecules for which temperature dependence data are now available, the hyperpolarizability contribution to $_mC$ is of opposite sign to that of the orientational term; consequently, the values of $\Delta\chi$ or $\Delta\alpha$ derived from temperature dependence studies are larger in magnitude than those estimated assuming $\Delta\eta = 0$. To date, there is no explanation for this behaviour, and it would be hazardous to assume that it is typical of other diamagnetic molecules. Theoretical calculations[9] of this property have only recently appeared for simple species, and the agreement with experimental values is promising.

For the methyl halides, the magnetic anisotropies derived using values of the polarizability anisotropies, known from Rayleigh light scattering work, were compared with those determined using other techniques, in particular the microwave Zeeman effect and NMR spectroscopy, with the aim of establishing a comparison of results from the three methods. The agreement amongst values of $\Delta\chi$ obtained from the three methods was generally satisfactory.

TABLE 8.1   MAGNETIC HYPERPOLARIZABILITY ANISOTROPIES [a] AND

THEIR RELATIVE CONTRIBUTIONS TO $_mC$ AT 300 K

Molecule	$10^{50}\Delta\eta$ / $C\,m^2V^{-1}T^{-2}$	% contribution	Ref.
Helium	0.2 ± 0.2	100	3
Neon	0.6 ± 0.5	100	3
Argon	3.9 ± 0.2	100	3
Krypton	6.7 ± 0.4	100	3
Xenon	16 ± 1	100	3
Hydrogen	2.3 ± 0.3	40	2
Deuterium	2.3 ± 0.5	40	2
Methane	7.2 ± 0.5	100	3
Methyl fluoride	2 ± 15	−4	
Methyl chloride	50 ± 35	−13	4
Methyl bromide	70 ± 15	−14	
Methyl iodide	100 ± 50	−13	
Chloroform	150 ± 70	−15	4
Carbon tetrachloride	80 ± 25	100	4
Ethane	2 ± 8	−3	
Ethylene	−2 ± 7	−1	
Acetylene	3 ± 8	−2	
Cyclopropane	−20 ± 20	−10	5

Table 8.1 continues on next page

Nitrogen	14 ± 10	−8	6
Carbon monoxide	1 ± 9	−1	6
Nitrous oxide	30 ± 20	−3	6
Sulfur dioxide	−15 ± 30	−5	7
Carbon dioxide	10 ± 15	−3	
Carbonyl sulfide	15 ± 20	−1	
Carbon disulfide	200 ± 70	−4	
Dimethyl ether	15 ± 20	−6	
Dimethyl sulfide	30 ± 30	−10	
Oxirane	85 ± 25	−40	
Furan	100 ± 30	−3	
Thiophene	180 ± 250	−3	
Pyridine	540 ± 400	5	
Benzene	−400 ± 300	−4	8
1,3,5-Trifluorobenzene	−75 ± 450	−1	8
Hexafluorobenzene	−15 ± 150	−0	8

(a) All values quoted were measured at $\lambda = 632.8$ nm. Unless otherwise indicated, the data are from the present study.

For molecules with three unique principal polarizabilities, the components of the polarizability were evaluated from a combination of the temperature dependence of the Cotton-Mouton effect, the magnetizabilities obtained from microwave Zeeman effect studies, the Rayleigh depolarization ratio and the mean polarizability. In such a procedure, the mean polarizability, the Rayleigh depolarization ratio and the Cotton-

Mouton constant must refer to the same optical frequency, and two possible sets of polarizability components are obtained due to the form of the expression for κ^2 (see equation (1.13)). For dimethyl ether, dimethyl sulfide, oxirane, furan and thiophene, the ambiguity in the results was resolved by comparison of each of the possible sets of polarizability components with ab initio results. The theoretical predictions were considered to be underestimates of the real values, due primarily to the neglect of vibrational averaging effects in the calculations. For each of these species, it was found that one of the possible sets of experimental polarizabilities could be disregarded, due to complete disagreement with the set of scaled theoretical values. A study of the temperature dependence of the Kerr effect provided an unambiguous set of polarizabilities for dimethyl ether, and the agreement of the polarizabilities determined from the three methods (that is, two experimental and one theoretical) was excellent.

Disagreement of results from considerably improved theoretical procedures and other experimental techniques led to a reinvestigation of the Cotton-Mouton effect of acetylene. The revised value of the magnetic anisotropy was significantly less negative than previously reported, and, consequently, the value of the quadrupole moment was much smaller. The agreement of the values of the magnetic anisotropy and the quadrupole moment determined here with results from other experimental and theoretical methods was also excellent, thereby establishing the reliability of the present technique and emphasizing the importance of including the effects of vibrational averaging in theoretical calculations.

The temperature dependences of the Cotton-Mouton effects of carbon dioxide, carbonyl sulfide and carbon disulfide provided useful comparisons with the results of the only other group currently active in this field. The values of the magnetic anisotropies of these species were obtained using the known Rayleigh depolarization

ratios, and the agreement of results from the two groups was excellent. However, the magnetic hyperpolarizability anisotropies were not in agreement, although these values were poorly determined due to the long extrapolation to $T^{-1} = 0$; and they were virtually negligible in comparison with the room temperature Cotton-Mouton constants.

Due to the uncertainty surrounding the values of the polarizability anisotropy of ethane (derived from studies of Rayleigh scattering, the temperature dependence of the Cotton-Mouton effect, the microwave Zeeman effect of CH_3CD_3 and the Stark effect of CH_3CD_3), it was considered worthwhile to re-examine the temperature dependence of the Cotton-Mouton effect of ethane. The analysis of the Cotton-Mouton effect data, combined with results from a recent study of the temperature dependence of the electric field-gradient induced birefringence offered a hitherto unused route to the polarizability anisotropy. The agreement with the values of the polarizability anisotropy derived from Rayleigh light scattering work adds support to those studies which exclude the contributions from vibrational Raman scattering, particularly for molecules which have very small Rayleigh depolarization ratios, as is the case for ethane. Conversely, conventional Rayleigh scattering studies of ethane have produced values of the polarizability anisotropy which are obviously too high. A value of the static polarizability anisotropy was determined using infrared intensities and light-scattering dispersion data. This value was in disagreement with a result derived from the study of the Stark effect, and this discrepancy deserves further investigation.

The two appendices contain discussions of results obtained for the temperature dependences of the Cotton-Mouton effects of pyridine and ethylene. The polarizability components of pyridine were determined from an analysis of the Cotton-Mouton effect data, the Rayleigh depolarization ratio, the mean polarizability, and the magnetizabilities, a procedure similar to that used for dimethyl ether and

related molecules. Once again, the ambiguity in the results was resolved by comparison with ab initio values, and the agreement with the values determined from the Kerr effect is, at best, fair, owing to the relatively low precision of the data. The polarizability components of ethylene were determined from an analysis of the Cotton-Mouton effect data, the polarizability tensor ratio, R_{20}, the mean polarizability, and the magnetizabilities. The single set of polarizabilities is in excellent agreement with ab initio values. Using infrared intensities and light-scattering dispersion data, the static polarizabilities were estimated, and these are in disagreement with those determined from the Stark effect; this discrepancy also deserves further investigation.

It is clear from the results presented here that the temperature dependence of the Cotton-Mouton effect of gas- and vapour-phase species is an extremely useful technique for the determination of several fundamental molecular properties. This experiment is particularly useful when the results are analyzed in conjunction with those from measurements of other optical effects (some of which include Rayleigh light scattering, electric-field and electric field-gradient induced birefringences), to obtain reliable values of various electric and magnetic properties. An important aspect of obtaining reliable experimental values of these properties lies in the increasing number of high-level theoretical calculations, and the need for comparisons as a test of these computations. There is considerable scope for measurements of other species of interest, such as borazine and substituted borazines, and the boron and phosphorus halides, for which there is a notable lack of data. It is hoped that the work described here, and the excellent equipment which is now available, will provide the impetus and a guide for further studies.

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