

## CHAPTER 4 - TEMPERATURE DEPENDENCE OF THE FIELD GRADIENT BIREFRINGENCE EFFECTS OF CARBON DIOXIDE AND CARBON DISULFIDE

### 4.1 INTRODUCTION

The molecular quadrupole moments of carbon dioxide and carbon disulfide have attracted much interest over the past thirty years, as indicated by the many published results. These results have been obtained using a wide variety of techniques, which include the field gradient birefringence effect,<sup>1-4</sup> dielectric and pressure virial coefficients,<sup>5</sup> far-infrared absorption<sup>6,7</sup> and theoretical calculations.<sup>8,9</sup> However, due to inconsistencies between these results, most of which were obtained using indirect methods, there are still no definitive values of the quadrupole moments for carbon dioxide and carbon disulfide.

In the case of carbon dioxide, it was of interest to see the controversy that arose, concerning the magnitude of the quadrupole moment, from the recent field gradient birefringence measurement by Graham *et al.*<sup>3</sup> These authors reported a value that was 10% lower than the previous result reported by Battaglia *et al.*,<sup>2</sup> thus casting doubt on the true magnitude of the quadrupole moment. Nearly all of the results published for carbon dioxide point towards the higher value of the quadrupole moment, but, because most of these are only approximate values and many rely on assumptions relating to intermolecular forces, the lower value could not be ruled out. Consequently, one of the aims of this study was to resolve this discrepancy.

Also, very little experimental information relating to the size of the quadrupole hyperpolarizability of carbon dioxide and carbon disulfide has been reported. One

previous study of the temperature dependence of the field gradient birefringence effect of carbon dioxide has been performed by Battaglia *et al.*,<sup>2</sup> who were able to separate the temperature-independent term from the larger orientational term. Thus they obtained a value for both the quadrupole moment and the hyperpolarizability. Some uncertainty arises in their results, however, as their value of  $-(14.98 \pm 0.5) \times 10^{-40} \text{ C m}^2$  for the quadrupole moment is larger than the estimate of  $-(14.67 \pm 0.26) \times 10^{-40} \text{ C m}^2$  obtained from their room-temperature measurement<sup>10</sup> where the contribution of the hyperpolarizability term is assumed to be negligible. As the temperature-independent term and the orientational term have the same sign for carbon dioxide, the magnitude of the quadrupole moment should decrease, rather than increase, when the two terms are separated. This point will be discussed further in Section 4.3. Other estimated values of the quadrupole hyperpolarizability have come from theoretical calculations.<sup>8,9</sup>

With a clear need to establish definitive values for the quadrupole moments and quadrupole hyperpolarizabilities of carbon dioxide and carbon disulfide, the temperature dependences of the field gradient birefringence effect were measured for these two compounds. The results are reported and discussed in the following sections.

## 4.2 EXPERIMENTAL

Measurements were performed on samples as follows: carbon dioxide (C.I.G. anaerobic grade, purity > 99.95%) used without purification; carbon disulfide (BDH Chemicals i.r. grade, purity > 99.9%), shaken with three portions of KMnO<sub>4</sub> solution, twice with mercury and finally with a solution of HgSO<sub>4</sub>; dried with CaCl<sub>2</sub> and fractionally distilled from P<sub>2</sub>O<sub>5</sub>. Each compound was analyzed by gas chromatography. The sample of carbon disulfide was subjected to three freeze-pump-thaw cycles prior to use.

The results are summarized in Tables 4.1 and 4.2 in which the uncertainties given for values of  ${}_mQ$  are the statistical uncertainties. Systematic errors discussed in previous chapters are not included in these values. Gas densities have been calculated from measured gas pressures and temperatures using published density virial coefficients.<sup>11</sup>

Although the apparatus is capable of withstanding gas pressures up to  $\approx 3500$  kPa, gas pressures for carbon dioxide were kept below 650 kPa to minimize beam bending at the higher temperatures. The size of the observed birefringence was found to be more than adequate under these conditions, as indicated by the precision of the results.

### 4.3 DISCUSSION

For a linear non-dipolar molecule, the expression for the molar field gradient birefringence constant can be written as

$${}_mQ = \frac{2N_A}{45\epsilon_0} \left\{ \frac{15}{2} B + \frac{\Delta\alpha\Theta}{kT} \right\} \quad (4.1)$$

where  $\Delta\alpha = \alpha_{zz} - \alpha_{xx}$  is the optical frequency polarizability anisotropy and the  $z$ -axis is coincident with the symmetry axis of the molecule. A linear dependence of  ${}_mQ$  on  $T^{-1}$  is predicted by equation 4.1, and this was indeed observed in the plots of the temperature dependences shown in Figures 4.1 and 4.2. For each molecule, the data were fitted to a first order polynomial in  $T^{-1}$  and the parameters of the least square fits are presented in Table 4.3.

In order to extract the quadrupole moments and quadrupole hyperpolarizabilities, respectively, for carbon dioxide and carbon disulfide from the slopes and intercepts of the graphs, accurate values of the polarizability anisotropies

TABLE 4.1 FIELD GRADIENT BIREFRINGENCE EFFECT OF CARBON DIOXIDE AT 632.8 nm

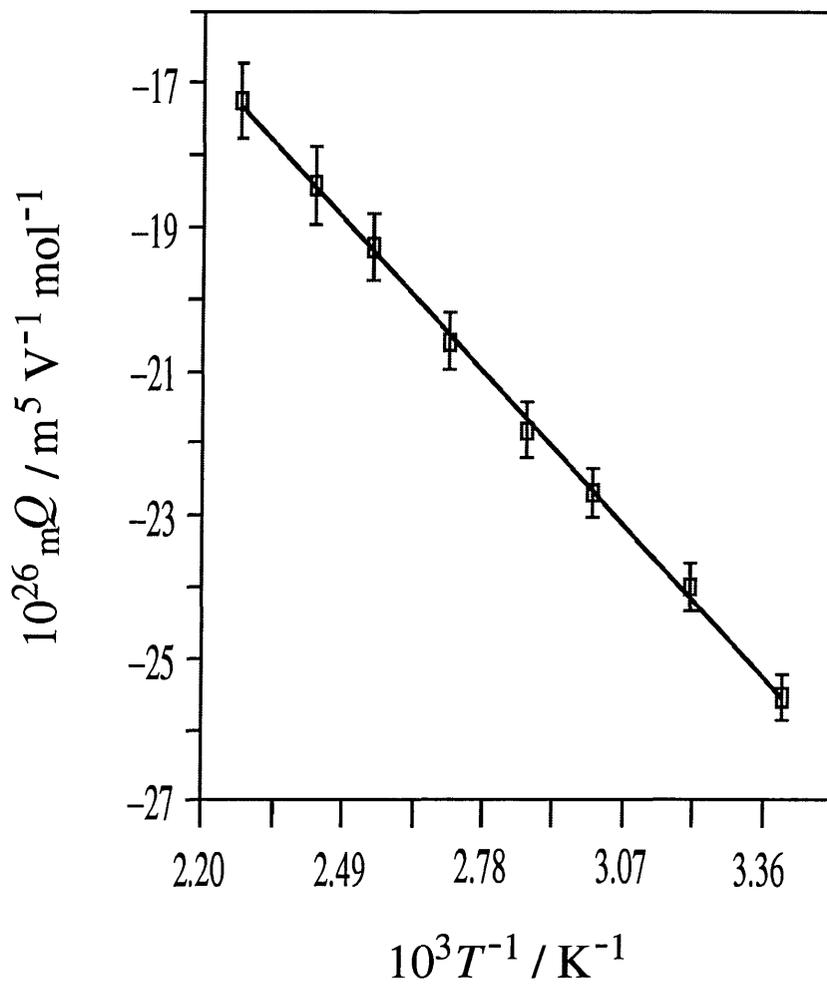
$T / \text{K}$	No. Runs	$p_{\text{max}} / \text{kPa}$	$10^6 B / \text{m}^3 \text{mol}^{-1}(\text{a})$	No. Measurements	$10^{26} {}_m Q / \text{m}^5 \text{V}^{-1} \text{mol}^{-1}$
294.2	8	610.4	- 123	80	- 25.55 ± 0.34
312.2	5	615.7	- 111	50	- 24.01 ± 0.41
333.2	6	513.1	- 97	60	- 22.70 ± 0.35
349.2	5	601.7	- 86	50	- 21.82 ± 0.42
369.2	6	553.6	- 76	60	- 20.59 ± 0.45
392.2	6	519.4	- 65	60	- 19.28 ± 0.43
412.2	6	326.3	- 56	60	- 18.42 ± 0.45
439.2	6	437.2	- 47	60	- 17.24 ± 0.46

(a) Reference 11

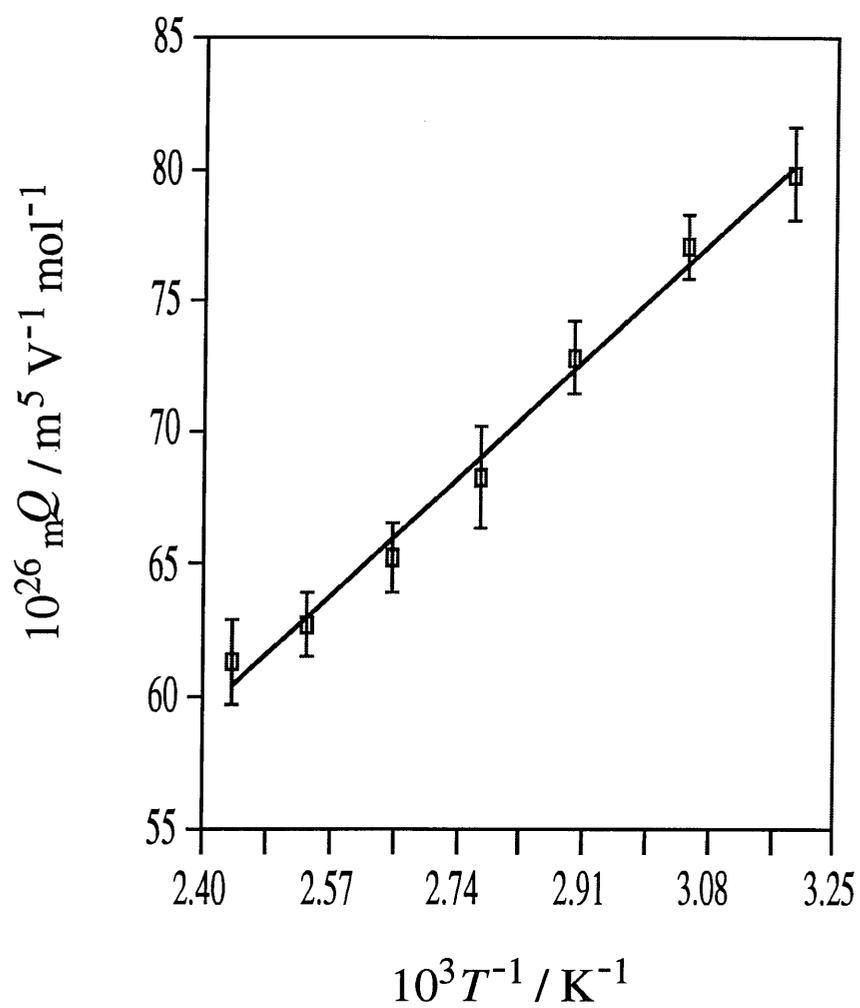
TABLE 4.2 FIELD GRADIENT BIREFRINGENCE EFFECT OF CARBON DISULFIDE AT 632.8 nm

$T / \text{K}$	No. Runs	$p_{\text{max}} / \text{kPa}$	$10^6 B / \text{m}^3 \text{mol}^{-1} \text{(a)}$	No. Measurements	$10^{26} {}_m Q / \text{m}^5 \text{V}^{-1} \text{mol}^{-1}$
313.2	7	34.15	- 725	70	$79.8 \pm 1.8$
328.2	7	46.77	- 654	70	$77.0 \pm 1.2$
345.2	7	48.31	- 587	70	$72.8 \pm 1.4$
361.2	7	45.61	- 533	70	$68.3 \pm 1.9$
377.2	7	50.35	- 484	70	$65.3 \pm 1.3$
394.2	7	50.43	- 443	70	$62.7 \pm 1.2$
410.2	7	50.00	- 411	70	$61.3 \pm 1.6$

(a) Reference 11



**Figure 4.1** Temperature dependence of the field gradient birefringence effect of carbon dioxide.



**Figure 4.2** Temperature dependence of the field gradient birefringence effect of carbon disulfide.

TABLE 4.3 ANALYSIS OF THE FIELD GRADIENT BIREFRINGENCE EFFECTS OF CO<sub>2</sub> AND CS<sub>2</sub>

Property	CO <sub>2</sub>	Value	CS <sub>2</sub>
$10^{26}$ intercept / m <sup>5</sup> V <sup>-1</sup> mol <sup>-1</sup>	- 0.62 ± 0.29		- 4.6 ± 3.0
$10^{23}$ slope / m <sup>5</sup> V <sup>-1</sup> K mol <sup>-1</sup>	- 7.34 ± 0.10		26.6 ± 1.1
$10^{60}B / C^3$ m <sup>4</sup> J <sup>-2</sup>	- 0.27 ± 0.13		- 2.0 ± 1.3
$10^{40}\Theta / C$ m <sup>2</sup>	- 14.3 ± 0.6		11.5 ± 0.5
$10^{40}\Delta\alpha / C^2$ m <sup>2</sup> J <sup>-1</sup> (a)	2.35 ± 0.07		10.53 ± 0.31
$10^{29} \Delta\chi / J T^{-2}$	- 10.4 ± 0.4		- 28.8 ± 1.3
$g_{\perp}$ (b)	- 0.05508 ± 0.00005		- 0.02274 ± 0.00002
$10^{47}I / kg$ m <sup>2</sup>	71.728 (c)		247.909 (d)
(a) Reference 12	(b) Reference 13	(c) Reference 14	(d) Reference 15

were needed. Carbon dioxide has been extensively studied and the value of  $\Delta\alpha = (2.35 \pm 0.07) \times 10^{-40} \text{ C}^2 \text{ m}^2 \text{ J}^{-1}$  from Rayleigh light scattering is known to be very reliable. Unfortunately, less work has been performed on carbon disulfide and the value of  $\Delta\alpha = (10.53 \pm 0.31) \times 10^{-40} \text{ C}^2 \text{ m}^2 \text{ J}^{-1}$  reported by Bogaard *et al*<sup>12</sup> is preferred in the present analysis.

The derived molecular properties for carbon dioxide and carbon disulfide are given in Table 4.3. The experimentally derived hyperpolarizabilities,  $B_{\text{CO}_2} = -(0.27 \pm 0.13) \times 10^{-60} \text{ C}^3 \text{ m}^4 \text{ J}^{-2}$  and  $B_{\text{CS}_2} = -(2.0 \pm 1.3) \times 10^{-60} \text{ C}^3 \text{ m}^4 \text{ J}^{-2}$ , are consistent with the theoretical prediction that the hyperpolarizability for carbon dioxide,<sup>9</sup>  $B = -0.36 \times 10^{-60} \text{ C}^3 \text{ m}^4 \text{ J}^{-2}$ , is an order of magnitude smaller than the value for carbon disulfide,<sup>10</sup>  $B = -2.68 \times 10^{-60} \text{ C}^3 \text{ m}^4 \text{ J}^{-2}$ . At 300 K, the relative contributions to  ${}_m Q$  arising from  $B$  are CO<sub>2</sub>,  $(2.4 \pm 1.2)\%$  and CS<sub>2</sub>,  $-(5.4 \pm 3.5)\%$ .

The present results for carbon dioxide are in reasonable agreement with those from the previous temperature-dependence study by Battaglia *et al*.<sup>2</sup> A comparison of the results is given in Table 4.4. It can be seen that the contribution of the hyperpolarizability term is found to be negligible in both studies. As one would expect, the molecular quadrupole moment derived in this study is smaller in magnitude (when the hyperpolarizability term is separated from the orientational term) than the estimated quadrupole moment from a single measurement at room temperature. However, this was not found in the study by Battaglia *et al*, where the size of the quadrupole moment increases when the hyperpolarizability term is separated out.

A further comparison of this present result with other values of the quadrupole moment for carbon dioxide obtained from various sources is given in Table 4.5. The present value removes any doubt as to the magnitude of the molecular quadrupole moment. Comparing the previous single-temperature measurements of the field gradient birefringence effect in carbon dioxide, it is clear that the recent result reported

by Graham *et al*<sup>3</sup> is an underestimate and is in error. This point is further confirmed by the theoretical calculation of Maroulis and Thakkar,<sup>8</sup> which yielded a value of  $\Theta = -(14.5 \pm 0.50) \times 10^{-40} \text{ C m}^2$ . Although the effects of vibrational averaging have been excluded from the calculations, the result is expected to be reliable. Also, several indirect methods, such as dielectric and pressure virial coefficients<sup>5</sup> and collision-induced far-infrared absorption,<sup>6,7</sup> have produced results in good agreement.

TABLE 4.4 STUDIES OF THE TEMPERATURE DEPENDENCE OF THE FIELD GRADIENT BIREFRINGENCE EFFECT OF CARBON DIOXIDE

	$10^{40} \left( \Theta + \frac{15BkT}{2\Delta\alpha} \right) / \text{C m}^2$	$10^{60} B / \text{C}^3 \text{ m}^4 \text{ J}^{-2}$	$10^{40} \Theta / \text{C m}^2$
present work	$-14.56 \pm 0.20$	$-0.27 \pm 0.13$	$-14.3 \pm 0.6$
Battaglia <i>et al</i>	$-14.67 \pm 0.26$	$-0.2 \pm 0.3$	$-14.98 \pm 0.50$

In the case of carbon disulfide, only a few measurements of the quadrupole moment have been reported and these are compared with the present result in Table 4.6. The investigations to date have produced discordant results, with the most reliable values coming from gas- and solution-phase measurements of the field gradient birefringence effect. These values, however, suffer from the assumption that the contribution of the temperature-independent term is negligible. This present study reveals that the hyperpolarizability term accounts for  $-6\%$  of the observed birefringence at room temperature and therefore needs to be considered to obtain a reliable value. From Table 4.6, the best agreement occurs between the result from this study and the value from the previous gas-phase measurement by Battaglia *et al*.<sup>2</sup> A theoretical calculation by Maroulis<sup>9</sup> also supports this present value. The derived values from methods such as second virial coefficients have been shown to be unreliable.

TABLE 4.5 COMPARISON OF VALUES OF THE MOLECULAR QUADRUPOLE  
MOMENT OF CARBON DIOXIDE

Method	$10^{40}\Theta / \text{C m}^2$	Ref
field gradient birefringence, temperature dependence	$-14.3 \pm 0.6$	present work
field gradient birefringence, temperature dependence	$-14.98 \pm 0.50$	2
field gradient birefringence, single temperature ( $B = 0$ )	$-14.3 \pm 0.7$	1
field gradient birefringence, single temperature ( $B = 0$ )	$-13.4 \pm 0.4$	3
collision-induced far i.r. absorption	$-14.3 \pm 1.3$	6
collision-induced far i.r. absorption	$-14.9 \pm 0.7$	7
dielectric and pressure virial coefficients	$-14.4$	5
ion scattering	$-14.7$	16
MBPT calculation	$-14.5 \pm 0.5$	8

TABLE 4.6 COMPARISON OF VALUES OF THE MOLECULAR QUADRUPOLE  
MOMENT OF CARBON DISULFIDE

Method	$10^{40}\Theta / \text{C m}^2$	Ref
field gradient birefringence, temperature dependence	$11.5 \pm 0.5$	present work
field gradient birefringence, single temperature ( $B = 0$ )	$12.0 \pm 0.6$	2
field gradient birefringence, solution phase	$14.2 \pm 1.1$	4
microwave line broadening	6.0	17
second virial coefficient	22.7	18
<i>Ab initio</i> calculation	11.0	19
SCF calculation	10.9	9

To examine the trend in the sign and magnitude of the quadrupole moment from carbon dioxide to carbon disulfide, it is also of interest to consider the quadrupole moment for carbonyl sulfide. An attempt was made in this study to measure the temperature dependence of the field gradient birefringence effect of carbonyl sulfide, but, the observed birefringence, even at room temperature, was too small to allow  ${}_mQ$  to be determined accurately, thereby making it impossible to obtain a reliable value of the quadrupole moment of carbonyl sulfide. Table 4.7 contains a summary of values for the quadrupole moment of carbonyl sulfide obtained from the microwave Zeeman effect. The values presented in Table 4.7 refer to the centre of mass quadrupole moment and not the effective quadrupole moment, due to carbonyl sulfide possessing a permanent dipole moment. However, the difference between the two values is expected to be small due to the small dipole moment of carbonyl sulfide. The most recent value of  $\Theta = -(2.58 \pm 0.08) \times 10^{-40} \text{ C m}^2$  reported by Taft *et al* <sup>20</sup> will be used in the following discussion.

TABLE 4.7 QUADRUPOLE MOMENTS FOR OCS FROM THE MICROWAVE  
ZEEMAN EFFECT

$10^{40}\Theta / C m^2$	Ref
$-2.58 \pm 0.08$	20
$-7.00$	21
$-2.94 \pm 0.50$	22
$-2.62 \pm 0.05$	23

Based on electronegativity arguments, a negative quadrupole polarization along the symmetry axis of each molecule is expected, yet measurements yield a positive value for carbon disulfide. One explanation of the change in sign of the quadrupole moment for carbon dioxide through to carbon disulfide was presented by Battaglia *et al.*<sup>2</sup> They rationalized the opposite signs in terms of the contributions from the nuclear and electronic parts of the  $\sigma$  and  $\pi$  molecular valence orbitals to the quadrupole moment. *Ab initio* calculations were used to investigate the molecular orbital contributions. From the subsequent analysis, it was found that the difference between the quadrupole moments of carbon dioxide and carbon disulfide may be attributed to the much greater contribution of the  $\pi$  valence orbitals in carbon disulfide.

A second investigation of the trend in the quadrupole moment for the series carbon dioxide, carbonyl sulfide and carbon disulfide was presented by Laidig.<sup>24</sup> By partitioning the molecular quadrupole moment into atomic contributions using the theory of atoms in molecules, Laidig obtained an in-depth understanding of the origin of the sign and magnitude of the molecular quadrupole moment. These contributions are based upon the spatial distribution of the charge density within each atom of the molecule. The necessary atomic contributions that are used in this approach are derived

from theoretical calculations with the aid of several software packages that are described elsewhere.<sup>24</sup> With the observed trend in the sign of the quadrupole moment due to the decreased charge transfer away from carbon as oxygen is replaced by sulfur through the series, this study shows that the positive value of the quadrupole moment for carbon disulfide results from the molecular charge distribution being flattened along and distributed away from the molecular axis.

The quadrupole moments for carbon dioxide and carbon disulfide can be used to provide an approximate value for the quadrupole moment of carbonyl sulfide, using an additivity scheme. Taking the mean of the values for carbon dioxide and carbon disulfide from this study, a value of  $\Theta = - (1.4 \pm 0.8) \times 10^{-40} \text{ C m}^2$  is obtained. Buckingham *et al*<sup>25</sup> reported a value for the quadrupole moment of carbonyl sulfide,  $\Theta = - (1.0 \pm 0.3) \text{ C m}^2$ , estimated from a single-temperature measurement of the field gradient birefringence effect. Adjusting this result for a more reliable value of the polarizability anisotropy,<sup>12</sup>  $\Delta\alpha = (4.53 \pm 0.13) \times 10^{-40} \text{ C}^2 \text{ m}^2 \text{ J}^{-1}$ , gives  $\Theta = - (1.3 \pm 0.4) \times 10^{-40} \text{ C m}^2$ . However, this value still suffers from the assumption that the quadrupole hyperpolarizability is zero, which, as shown by this study, is not valid. An estimated value of the hyperpolarizability for carbonyl sulfide, calculated from the mean of the values for carbon dioxide and carbon disulfide, is  $B_{OCS} = - (1.1 \pm 1.3) \times 10^{-60} \text{ C}^3 \text{ m}^4 \text{ J}^{-2}$ . Thus, allowing for the hyperpolarizability, the derived value for the effective quadrupole moment of carbonyl sulfide is  $\Theta = - (0.5 \pm 1.0) \times 10^{-40} \text{ C m}^2$ . This value is in fair agreement with the above value of  $\Theta = - (1.4 \pm 0.8) \times 10^{-40} \text{ C m}^2$ . Using the known value of the dipole moment for carbonyl sulfide,<sup>22</sup>  $\mu = 2.50 \times 10^{-30} \text{ C m}$ , and assuming the derived effective quadrupole moment to be reliable, the position of the effective quadrupole centre can be determined from equation (1.36). Substituting in the above values for  $\mu$ ,  $\Theta_{EQC}$  and  $\Theta_{CM}$ , gives  $Z = - 4.1 \times 10^{-11} \text{ m}$ . Thus, taking  $Z$  to be positive in the O→S direction, the effective quadrupole centre is located 0.011 nm from the central carbon atom, along the C–S bond.

The magnetic anisotropies for carbon dioxide and carbon disulfide, shown in Table 4.3, were obtained directly using the quadrupole moments from the present work with rotational constants and molecular  $g$  values from microwave spectroscopy. These values are compared with previous estimates in Table 4.8.

TABLE 4.8 THE MAGNETIC ANISOTROPIES FOR CO<sub>2</sub> AND CS<sub>2</sub>

Method	CO <sub>2</sub> ( $\times 10^{-29} \text{ J T}^{-2}$ )	CS <sub>2</sub> ( $\times 10^{-29} \text{ J T}^{-2}$ )
present work	$-10.4 \pm 0.4$	$-28.8 \pm 1.3$
magnetic birefringence, <sup>(a)</sup> temperature dependence	$-10.5 \pm 0.3$	$-30.7 \pm 1.3$

(a) Reference 26

It can be seen that there is good agreement between the present derived values and those obtained from the temperature dependences of the Cotton-Mouton effect.

The above analysis of the field gradient birefringence effects of carbon dioxide and carbon disulfide has provided definitive values for the molecular quadrupole moments and quadrupole hyperpolarizabilities. In particular, the results for carbon dioxide resolve the discrepancy over the true magnitude of the quadrupole moment. This study has shown that the contribution of the quadrupole hyperpolarizability to the observed birefringence at room temperature is very small for both of these molecules. Also, reliable values of the magnetic anisotropies have been obtained using the present results.

#### 4.4 REFERENCES

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## CHAPTER 5 - TEMPERATURE DEPENDENCE OF THE FIELD GRADIENT BIREFRINGENCE EFFECTS OF BENZENE AND HEXAFLUOROBENZENE

### 5.1 INTRODUCTION

For a considerable time, much effort has gone into determining the sign and magnitude of the molecular quadrupole moment of benzene and to a lesser extent hexafluorobenzene. With these molecules having no permanent dipole moment, the molecular quadrupole moment is an important property describing the electronic charge distribution of the molecule. Measurements of the field gradient birefringence effect of benzene and hexafluorobenzene in the vapour phase,<sup>1</sup> performed over a limited temperature range, enabled the sign and magnitude of the molecular quadrupole moments for these molecules to be calculated. However, some uncertainty attaches to these results as the workers assumed that the contribution from the temperature-independent term was negligible. As very little information concerning the quadrupole hyperpolarizabilities of these molecules is available, the validity of the above assumption remains to be determined.

Several liquid- and solution-phase measurements of the field gradient birefringence effects of these compounds have also been performed, yielding values of the molecular quadrupole moment.<sup>2,3</sup> These values not only rely on assumptions regarding the negligible contribution of the temperature-independent term, but also on assumptions relating to solute-solvent interactions, again making the results uncertain. Other experimental and theoretical methods have been used to determine the magnitude of the quadrupole moment for benzene. These include microwave line-broadening,<sup>4</sup>

second virial coefficients<sup>5-7</sup>, far infrared absorption<sup>8</sup> and SCF calculations.<sup>9,10</sup> As all of the results obtained from the methods mentioned above involve assumptions of some kind, some doubt must therefore be cast upon these values of the molecular quadrupole moment of benzene and hexafluorobenzene.

Consequently, the present study of the field gradient birefringence effect of benzene and hexafluorobenzene was undertaken for the following reasons: firstly, to obtain definitive values for the molecular quadrupole moments and quadrupole hyperpolarizabilities of benzene and hexafluorobenzene; and secondly, to determine if the contribution of the temperature-independent term to the birefringence is significant for these molecules.

## 5.2 EXPERIMENTAL

The measurements presented in this chapter were performed on samples in the temperature range from 319 K to 415 K. Benzene and hexafluorobenzene were both purified as follows: benzene (Aldrich HPLC grade, purity >99.9%) and hexafluorobenzene (Aldrich, purity >99%), fractionally distilled from phosphorous pentoxide. The final purities of the samples were checked by gas chromatography. In addition, each sample was subjected to three freeze-pump-thaw cycles and distilled *in vacuo* into the cell.

The experimental results are summarized in Tables 5.1 and 5.2. Measurements were performed at different pressures ranging from a minimum of 26.9 kPa to a maximum of 63.1 kPa at the higher temperatures. Vapour densities of benzene and hexafluorobenzene were calculated using recorded density virial coefficients.<sup>11</sup>

TABLE 5.1 FIELD GRADIENT BIREFRINGENCE EFFECT OF BENZENE AT 632.8 nm

$T / \text{K}$	No. Runs	$p_{\text{max}} / \text{kPa}$	$10^6 B / \text{m}^3 \text{mol}^{-1}(\text{a})$	No. Measurements	$10^{26} {}_m Q / \text{m}^5 \text{V}^{-1} \text{mol}^{-1}$
319.2	8	26.91	- 1241	104	$118.6 \pm 3.6$
334.2	8	39.37	- 1112	80	$112.2 \pm 3.6$
349.2	5	31.47	- 985	50	$107.0 \pm 3.0$
366.2	8	63.74	- 877	74	$101.9 \pm 2.6$
381.2	8	66.74	- 801	80	$97.4 \pm 2.4$
396.2	8	64.59	- 730	80	$93.5 \pm 2.6$
415.2	6	63.07	- 665	60	$88.0 \pm 2.4$

(a) Reference 11

TABLE 5.2 FIELD GRADIENT BIREFRINGENCE EFFECT OF HEXAFLUOROBENZENE AT 632.8 nm

$T / \text{K}$	No. Runs	$p_{\text{max}} / \text{kPa}$	$10^6 B / \text{m}^3 \text{mol}^{-1(\text{a})}$	No. Measurements	$10^{26} {}_{\text{m}}Q / \text{m}^5 \text{V}^{-1} \text{mol}^{-1}$
318.2	8	15.67	- 1999	80	- 146.0 ± 5.9
330.2	8	20.95	- 1773	80	- 141.8 ± 3.8
342.2	8	24.17	- 1604	80	- 139.6 ± 3.7
358.2	8	28.11	- 1397	80	- 134.7 ± 3.1
375.2	7	28.02	- 1193	70	- 129.2 ± 4.9
392.2	8	29.10	- 1050	80	- 123.3 ± 3.1
410.2	8	32.60	- 934	80	- 116.1 ± 2.8

(a) Reference 11

From the experiment, the observed retardances were sufficient in size for each of the substances, despite the low vapour pressures, and  ${}_mQ$  values were obtained to a high accuracy. The uncertainties in the values of  ${}_mQ$  reported in Tables 5.1 and 5.2 are the statistical errors associated with the noise of the experiment.

### 5.3 DISCUSSION

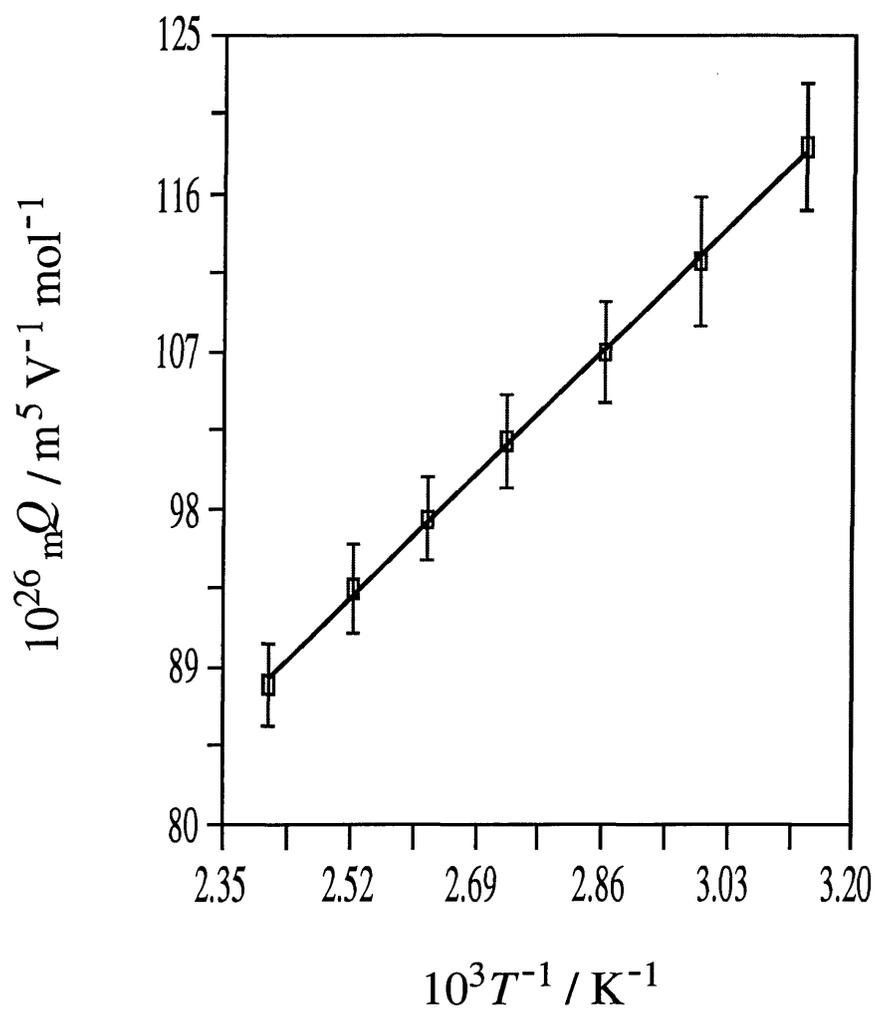
The temperature dependence of  ${}_mQ$  for non-dipolar molecules with  $D_{6h}$  symmetry is described by

$${}_mQ = \frac{2N_A}{45\epsilon_0} \left\{ \frac{15}{2}B + \frac{\Delta\alpha\Theta}{kT} \right\} \quad (5.1)$$

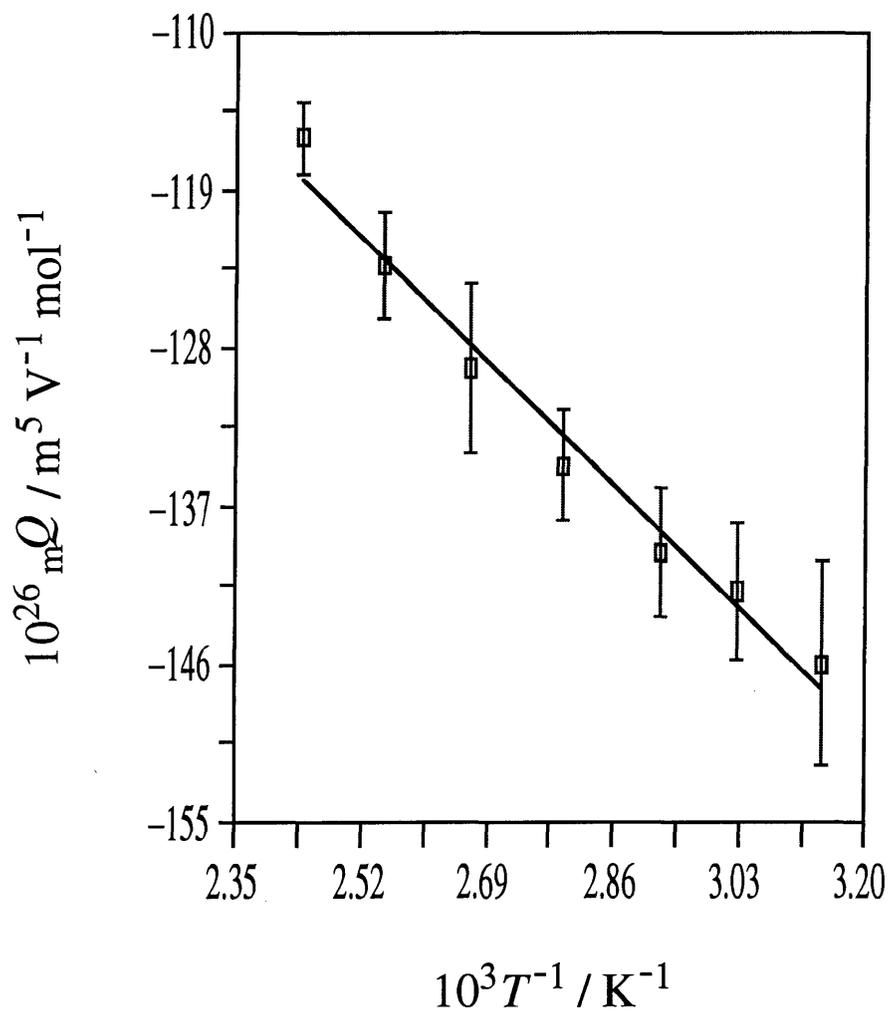
where the  $z$ -axis is coincident with the 6-fold axis of the molecule.

Equation 5.1 predicts a linear dependence of  ${}_mQ$  on  $T^{-1}$ , and plots of the temperature dependences, shown in Figures 5.1 and 5.2, verify this behaviour. The present values of  ${}_mQ$  at 298 K for benzene and hexafluorobenzene are compared in Table 5.3 with previous results reported by Battaglia *et al.*<sup>1</sup> The agreement shown between these values, for both molecules, is excellent. Table 5.4 contains an analysis of the temperature-dependence data and the derived molecular properties.

For each of these molecules, the contribution of the temperature-independent term to  ${}_mQ$  is relatively small, but still significant, when compared to the very much larger orientational term. At 300 K, the relative contributions of the hyperpolarizability term to  ${}_mQ$  are  $-(9.1 \pm 1.3)\%$  and  $(7 \pm 5)\%$ , for benzene and hexafluorobenzene, respectively. Thus, in order to obtain reliable values of the quadrupole moment for these molecules, the hyperpolarizability term must be taken into account.



**Figure 5.1** Temperature dependence of the field gradient birefringence effect of benzene.



**Figure 5.2** Temperature dependence of the field gradient birefringence effect of hexafluorobenzene.

TABLE 5.3 COMPARISON OF VALUES OF  ${}_mQ$  FOR BENZENE AND  
HEXAFLUOROBENZENE AT 298 K

Author	$C_6H_6$ ( $10^{26} {}_mQ / m^5 V^{-1} mol^{-1}$ )	$C_6F_6$ ( $-10^{26} {}_mQ / m^5 V^{-1} mol^{-1}$ )
present work	$128 \pm 4$	$-158 \pm 10$
Battaglia <i>et al</i> , <sup>(a)</sup> vapour phase	$133 \pm 8$	$-164 \pm 9$

(a) Reference 1

Consequently, the assumption made by Battaglia *et al*,<sup>1</sup> Vrbancich *et al*<sup>2</sup> and Dennis *et al*,<sup>3</sup> when determining the quadrupole moment, that the contribution from the hyperpolarizability term is negligibly small, is found to be doubtful.

Values of the polarizability anisotropies for benzene and hexafluorobenzene, used in the extraction of the molecular quadrupole moments from the slopes of  ${}_mQ$  against  $T^{-1}$ , were obtained from Rayleigh light scattering experiments performed at 632.8 nm.<sup>12</sup>

The derived molecular quadrupole moment for benzene shown in Table 5.4 is compared with previous estimates from various procedures in Table 5.5. It can be seen that the present value is in good agreement with those reported by Battaglia *et al*,<sup>1</sup> Vrbancich *et al*<sup>2</sup> and Dennis *et al*<sup>3</sup> using similar birefringence measurements. Thus the models treating the effects of the solvent environment used by Vrbancich *et al* and Dennis *et al* appear to be adequate in their treatment of the local field and reaction field gradient, as shown by the good agreement between the results. However, as no assumption was made in this present study regarding the contribution of the quadrupole hyperpolarizability, the present result may be considered to be the most reliable.

TABLE 5.4 ANALYSIS OF THE FIELD GRADIENT BIREFRINGENCE EFFECTS OF C<sub>6</sub>H<sub>6</sub> AND C<sub>6</sub>F<sub>6</sub>

Property	C <sub>6</sub> H <sub>6</sub>	Value	C <sub>6</sub> F <sub>6</sub>
$10^{26}$ intercept / m <sup>5</sup> V <sup>-1</sup> mol <sup>-1</sup>	- 11.7 ± 1.5		- 11.2 ± 7.8
$10^{23}$ slope / m <sup>5</sup> V <sup>-1</sup> K mol <sup>-1</sup>	41.5 ± 0.6		- 43.7 ± 2.9
$10^{60}B / C^3$ m <sup>4</sup> J <sup>-2</sup>	- 5.1 ± 0.7		- 4.9 ± 3.4
$10^{40}\Theta / C$ m <sup>2</sup>	- 30.4 ± 1.2		28.1 ± 1.8
$10^{40}\Delta\alpha / C^2$ m <sup>2</sup> J <sup>-1</sup> (a)	- 6.23 ± 0.18		- 7.09 ± 0.20
$10^{29} \Delta\chi / J$ T <sup>-2</sup> (b)	- 112.1 ± 4.3		- 66.0 ± 2.4
$g_{\parallel} - \frac{1}{2}g_{\perp}$	0.1009 ± 0.0034		0.00777 ± 0.00036
$10^{47}I_{\parallel} / \text{kg m}^2$	295.34 (c)		1638.17 (d)

(a) Reference 12

(b) Reference 13

(c) Reference 14

(d) Reference 15

Another relevant gas-phase study reported by Stolze *et al*,<sup>16</sup> yields a quadrupole moment which is in reasonable agreement with the present value. These investigators exploited an approach originally developed by Shoemaker and Flygare,<sup>17</sup> that enabled the quadrupole moment of benzene to be derived from measurements of the rotational Zeeman effect in fluorobenzene. This procedure assumes that the C-F bond is approximately axially symmetric and that the F atom does not distort the aromatic ring. Although the original value obtained by Shoemaker and Flygare of  $\Theta = -(18.7 \pm 9.4) \times 10^{-40} \text{ C m}^2$  has been shown to be an underestimate, Stolze and coworkers, using equipment with greater sensitivity and resolution, thereby obtaining more accurate  $g$  values and magnetic anisotropies, have shown this technique to be quite reliable.

TABLE 5.5 COMPARISON OF VALUES OF THE MOLECULAR QUADRUPOLE MOMENT OF BENZENE

Method	$10^{40}\Theta / \text{C m}^2$	Ref
field gradient birefringence, temperature dependence	$-30.4 \pm 1.2$	present work
field gradient birefringence, vapour phase ( $B = 0$ )	$-29.0 \pm 1.7$	1
field gradient birefringence, solution phase	$-28.3 \pm 1.2$	3
Zeeman effect	$-28.4 \pm 4.7$	16
Zeeman effect	$-18.7 \pm 9.4$	17
second virial coefficient	$-40.0$	7
far i.r. absorption	$-12.7$	8
<i>Ab initio</i> calculation	$-29.3 \text{ --- } -30.7$	18

*Ab initio* calculations on benzene have been limited due to the size of the molecule. Several values have been reported ranging from  $-28.6 \times 10^{-40} \text{ C m}^2$ <sup>9</sup> to  $-34.7 \times 10^{-40} \text{ C m}^2$ <sup>10</sup> depending on the size and accuracy of the basis sets employed in the calculations. A calculation by Ha,<sup>18</sup> using CI wavefunctions, produced a value for the molecular quadrupole moment in the range of  $(-29.3 - 30.7) \times 10^{-40} \text{ C m}^2$ .

Similarly, Table 5.6 compares the derived molecular quadrupole moment for hexafluorobenzene with previous estimates obtained from the gas- and solution-phase field gradient birefringence effect by other workers. In comparison with benzene, very little work has been reported on the molecular quadrupole moment of hexafluorobenzene, which is surprising due to their similar molecular properties. From Table 5.6, there is reasonable agreement between all of the results, but the previous results suffer from the assumption that the quadrupole hyperpolarizability contribution is negligible. Thus the present result may again be considered to be the most reliable value for the molecular quadrupole moment of hexafluorobenzene.

TABLE 5.6 COMPARISON OF VALUES OF THE MOLECULAR QUADRUPOLE MOMENT OF HEXAFLUOROBENZENE

Method	$10^{40}\Theta / \text{C m}^2$	Ref
field gradient birefringence, temperature dependence	$28.1 \pm 1.8$	present work
field gradient birefringence, vapour phase ( $B = 0$ )	$31.7 \pm 1.7$	1
field gradient birefringence, solution phase	$31.7 \pm 1.7$	2

It has been suggested by previous workers<sup>1,2</sup> that it may be possible to estimate the molecular quadrupole moments for other fluorinated benzenes from the measured values for benzene and hexafluorobenzene. Unfortunately, for several reasons, it was not possible to determine the molecular quadrupole moment of 1,3,5-trifluorobenzene, in the gas phase, in this study. However, as Vrbancich *et al*<sup>2</sup> have measured  ${}_mQ$  for 1,3,5-trifluorobenzene in the solution phase, and, as their results for benzene and hexafluorobenzene are in good agreement with the present values, it should be reasonable to assume that their value for 1,3,5-trifluorobenzene,  ${}_mQ = -(14.6 \pm 1.8) \times 10^{-26} \text{ m}^5 \text{ V}^{-1} \text{ mol}^{-1}$ , is reliable.

As the measurement was performed at a single temperature it is necessary to account for the temperature-independent term in their  ${}_mQ$  value when calculating the quadrupole moment, so a proper comparison can be made. Using an average of the quadrupole hyperpolarizabilities for benzene and hexafluorobenzene derived in this work, a value of  $B = -(5.0 \pm 3.5) \times 10^{-60} \text{ C}^3 \text{ m}^4 \text{ J}^{-2}$  for 1,3,5-trifluorobenzene should be a reasonable approximation. This yields a value of the molecular quadrupole moment for 1,3,5-trifluorobenzene of  $\Theta = (0.7 \pm 1.8) \times 10^{-40} \text{ C m}^2$ . Taking the mean of the quadrupole moments for benzene and hexafluorobenzene to estimate the quadrupole moment of 1,3,5-trifluorobenzene, gives a quadrupole moment of  $\Theta = -(1.2 \pm 2.0) \times 10^{-40} \text{ C m}^2$  which is in reasonable agreement with the value for the quadrupole moment derived above. Thus the potential for estimating quadrupole moments from additivity schemes, has again been demonstrated.

The opposite signs of the quadrupole moments of benzene and hexafluorobenzene can be attributed to the change in the electronic charge distribution due to the fluorine substituents. Two different approaches to interpreting this fact have been presented in the literature. Vrbancich *et al*<sup>2</sup> rationalized their results in terms of the nuclear and electronic contributions to the quadrupole moment. For a molecule

possessing a 3-fold or higher-order axis of symmetry, the molecular quadrupole moment can be expressed as

$$\Theta = e \left\{ \sum_n Z_n (z_n^2 - x_n^2) \right\} - e \left\{ \langle z^2 \rangle - \langle x^2 \rangle \right\} \quad (5.2)$$

where  $e$  is the protonic charge,  $Z_n$  is the atomic number of the  $n^{\text{th}}$  nucleus and  $\langle z^2 \rangle - \langle x^2 \rangle$  is the anisotropy in the second moment of the electronic charge distribution. They suggested that the negative sign of the quadrupole moment for benzene indicates that electronic charge must be shifted slightly from the H-atoms and the H-C bonds towards and inside the periphery of the  $C_6$ -ring. Consequently  $\langle z^2 \rangle - \langle x^2 \rangle$  is less negative than if there were no interactions between the constituent atoms and hence the observed quadrupole moment is negative in sign. An analogous argument was applied to hexafluorobenzene, in which the highly electronegative F-atoms tend to localize electronic charge making the C-atoms slightly electron deficient. Thus  $\langle z^2 \rangle - \langle x^2 \rangle$  is more negative than if there were no interactions between the constituent atoms and the quadrupole moment is positive in sign.

A second approach by Laidig,<sup>19</sup> similar to the one presented in the previous chapter, is based on the theory of atoms in molecules. The results from this study indicate that although the electronic charge about the carbon atoms in both molecules has the same form, an oblate sphere centred along the  $z$ -axis (6-fold axis) and depleted along the axes of the molecular plane, it is the transfer of charge away from the molecular origin in hexafluorobenzene that results in the positive value of the molecular quadrupole moment and not an overall flattening of the charge throughout the molecule.

From the molecular quadrupole moments for benzene and hexafluorobenzene derived in this work, it is possible to determine reliable values of  $g_{\parallel} - \frac{1}{2}g_{\perp}$ , where  $g_{\parallel}$  and  $g_{\perp}$  are the  $g$  values relating the rotational magnetic moment to the angular

momentum. For a planar, symmetric top molecule,  $I_{\perp} = \frac{1}{2}I_{\parallel}$  and equation (1.45) reduces to

$$\Theta = -(eI_{\parallel}/M_P)\left(g_{\parallel} - \frac{1}{2}g_{\perp}\right) - (4m/e)\Delta\chi \quad (5.3)$$

In order to extract  $g_{\parallel} - \frac{1}{2}g_{\perp}$ , reliable values of the magnetic anisotropy for benzene and hexafluorobenzene are required. The following values (recalculated using the values of the polarizability anisotropies given in Table 5.4) were obtained from a study of the temperature dependence of the Cotton-Mouton effects<sup>13</sup> of these compounds:  $\Delta\chi(C_6H_6) = -(112.1 \pm 4.3) \times 10^{-29} \text{ J T}^{-2}$  and  $\Delta\chi(C_6F_6) = -(66.0 \pm 2.4) \times 10^{-29} \text{ J T}^{-2}$ . These values are considered the most reliable available, as they were derived from vapour-phase measurements, and made no assumptions relating to the contribution of the temperature-independent term to the observed effect. From equation (5.3), the derived values of  $g_{\parallel} - \frac{1}{2}g_{\perp}$  for benzene and hexafluorobenzene, are given in Table 5.4.

The present study of the temperature dependence of vapour-phase electric field gradient birefringence has demonstrated that for benzene and hexafluorobenzene the contributions of the quadrupole hyperpolarizabilities to the field gradient birefringence effects at normal temperatures are significant. In addition, reliable values of the molecular quadrupole moments have been obtained. These values, in combination with the known magnetic anisotropies and moments of inertia, were then used to determine the anisotropy in the  $g$  value.

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## CHAPTER 6 - TEMPERATURE DEPENDENCE OF THE FIELD GRADIENT BIREFRINGENCE EFFECTS OF ETHANE AND CYCLOPROPANE

### 6.1 INTRODUCTION

In previous chapters, it has been shown that the quadrupole hyperpolarizability contributions to the field gradient birefringence effect at 300 K for molecules with relatively large quadrupole moments are small (< 10%) compared to the orientational contributions. However, for molecules with small quadrupole moments, theoretical evidence <sup>1</sup> suggests that the hyperpolarizability term will contribute significantly (> 30%). Consequently measurements of  ${}_mQ$  as a function of temperature are necessary to separate the hyperpolarizability and orientational terms so that reliable values of the molecular quadrupole moment can be obtained. Ethane and cyclopropane, being weakly anisotropic molecules with small quadrupole moments, are excellent examples for such a study.

Two estimates of the quadrupole moment for ethane have come from single-temperature measurements of the field gradient birefringence effect.<sup>2,3</sup> These values were derived by assuming the quadrupole hyperpolarizability contribution to be negligible, thus making these results very doubtful. A similar case exists for cyclopropane where the previous measurement <sup>3</sup> assumed the quadrupole hyperpolarizability to be zero. Other methods that have been used to estimate the quadrupole moments of these molecules include collision-induced far-infrared absorption,<sup>4</sup> the microwave Zeeman effect <sup>5</sup> and theoretical calculations.<sup>6,7</sup>

Poor agreement between the few reported values of the molecular quadrupole moments for ethane and cyclopropane show that reliable results have not yet been obtained for these molecules. Also, there is a notable absence of information concerning the quadrupole hyperpolarizabilities of these molecules, apart from some theoretical estimates, calculated using small basis sets, that are known to be unreliable.<sup>1</sup> Thus for these reasons, the field gradient birefringence effects of these two molecules have been studied over a range of temperatures, and the results are reported and discussed in this chapter.

This present work is the first reported systematic investigation of the contribution of the quadrupole hyperpolarizability to the field gradient birefringence effect of molecules in this class.

## 6.2 EXPERIMENTAL

The sources and purities of the samples used were as follows: ethane (Matheson, purity > 99.0%); cyclopropane (C.I.G. medical grade, purity > 99.9%). Both samples were used without purification. Analyses of the samples by gas chromatography showed no significant impurities.

The measurements on these compounds are summarized in Tables 6.1 and 6.2. Relatively large gas pressures, in the range of 1000 – 1800 kPa were used for ethane, while pressures for cyclopropane were  $\approx$  500 kPa. Gas densities were calculated in the usual manner using published virial coefficients.<sup>8</sup> Although the induced birefringence exhibited by each compound was relatively small, it was possible to obtain well determined values of  ${}_mQ$  at each temperature, by taking more measurements with longer averaging times.

TABLE 6.1 FIELD GRADIENT BIREFRINGENCE EFFECT OF ETHANE AT 632.8 nm

$T / \text{K}$	No. Runs	$p_{\text{max}} / \text{kPa}$	$10^6 B / \text{m}^3 \text{mol}^{-1}(\text{a})$	No. Measurements	$10^{26} {}_m Q / \text{m}^5 \text{V}^{-1} \text{mol}^{-1}$
293.2	6	1097.3	- 193	60	- 2.03 ± 0.04
311.2	9	1733.4	- 170	118	- 1.98 ± 0.05
328.2	8	1236.5	- 150	104	- 1.93 ± 0.05
344.2	7	1257.9	- 136	90	- 1.84 ± 0.06
360.2	8	1275.5	- 122	104	- 1.83 ± 0.06
376.2	7	1307.2	- 111	90	- 1.74 ± 0.08
394.2	8	1323.5	- 100	80	- 1.70 ± 0.07
411.2	6	1768.8	- 92	68	- 1.63 ± 0.09

(a) Reference 8

TABLE 6.2 FIELD GRADIENT BIREFRINGENCE EFFECT OF CYCLOPROPANE AT 632.8 nm

$T / \text{K}$	No. Runs	$p_{\text{max}} / \text{kPa}$	$10^6 B / \text{m}^3 \text{mol}^{-1}(\text{a})$	No. Measurements	$10^{26} {}_m Q / \text{m}^5 \text{V}^{-1} \text{mol}^{-1}$
295.2	7	448.1	- 400	70	- 5.12 ± 0.14
311.2	7	507.1	- 351	70	- 4.90 ± 0.12
326.2	6	496.4	- 320	60	- 4.81 ± 0.14
344.2	7	511.9	- 280	70	- 4.72 ± 0.12
364.2	6	530.6	- 250	60	- 4.65 ± 0.16
378.2	6	542.1	- 229	60	- 4.53 ± 0.11
395.2	6	520.2	- 207	60	- 4.46 ± 0.14
412.2	6	530.1	- 190	60	- 4.35 ± 0.19

(a) Reference 8

### 6.3 DISCUSSION

For molecules with  $C_3$  symmetry, the molar field gradient birefringence constant may be expressed as

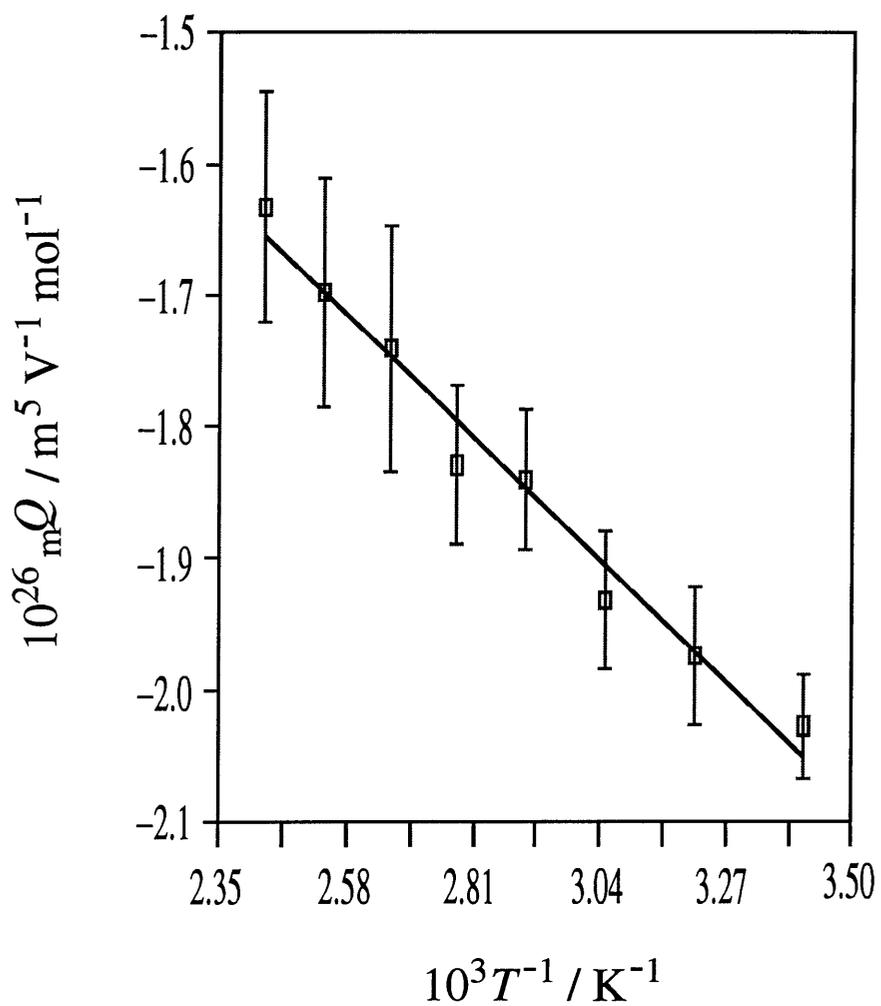
$${}_mQ = \frac{2N_A}{45\epsilon_0} \left\{ \frac{15}{2} B + \frac{\Theta\Delta\alpha}{kT} \right\} \quad (6.1)$$

where the  $z$ -axis is coincident with the  $C_3$  axis of the molecule.

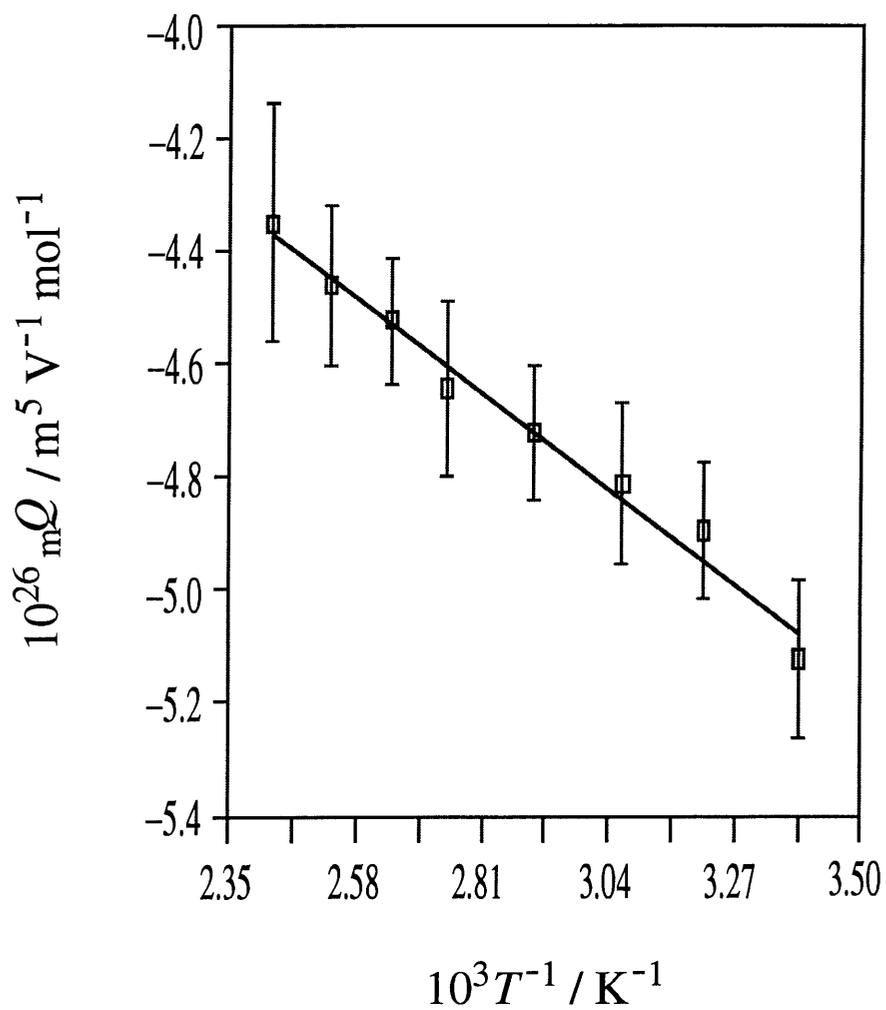
The temperature dependences of the observed  ${}_mQ$  values are illustrated in Figures 6.1 and 6.2. As expected, both graphs show a linear dependence on  $T^{-1}$ . The results of a weighted least-squares fitting procedure, together with a detailed analysis of the derived properties, are given in Table 6.3.

For ethane and cyclopropane, it can be seen from the values of the intercepts that the temperature-independent contributions to the observed birefringence are significant at normal temperatures. The relative contributions of the hyperpolarizability term to  ${}_mQ$  at 300 K are  $(37 \pm 5)\%$  for ethane and  $(52 \pm 3)\%$  for cyclopropane. Although these contributions are large, it must be emphasized that the magnitudes of these hyperpolarizabilities are relatively small when compared to the much larger value for benzene (presented in chapter 5), thus making their evaluation extremely difficult. The precision of the hyperpolarizabilities obtained for ethane and cyclopropane reflects the accuracy of the measurements performed on these molecules.

The polarizability anisotropies for these weakly anisotropic molecules were derived from depolarization ratios measured at 632.8 nm. The following values for ethane<sup>9</sup> and cyclopropane<sup>10</sup> were used in this analysis: ethane  $\Delta\alpha = (0.776 \pm 0.023) \times 10^{-40} \text{ C}^2 \text{ m}^2 \text{ J}^{-1}$  and cyclopropane  $\Delta\alpha = - (0.854 \pm 0.025) \times 10^{-40} \text{ C}^2 \text{ m}^2 \text{ J}^{-1}$ . Discrepancies between the reported values for these molecules<sup>11</sup> arise from the



**Figure 6.1** Temperature dependence of the field gradient birefringence effect of ethane.



**Figure 6.2** Temperature dependence of the field gradient birefringence effect of cyclopropane.

TABLE 6.3 ANALYSIS OF THE FIELD GRADIENT BIREFRINGENCE EFFECTS OF C<sub>2</sub>H<sub>6</sub> AND C<sub>3</sub>H<sub>6</sub>

Property	Value			
	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>6</sub>		
$10^{26}$ intercept / m <sup>5</sup> V <sup>-1</sup> mol <sup>-1</sup>	- 0.74 ± 0.08	- 2.61 ± 0.12		
$10^{23}$ slope / m <sup>5</sup> V <sup>-1</sup> K mol <sup>-1</sup>	- 0.382 ± 0.026	- 0.726 ± 0.042		
$10^{60}B / C^3$ m <sup>4</sup> J <sup>-2</sup>	- 0.327 ± 0.035	- 1.15 ± 0.05		
$10^{40}\Theta / C$ m <sup>2</sup>	- 2.25 ± 0.15	3.88 ± 0.23		
$10^{40}\Delta\alpha / C^2$ m <sup>2</sup> J <sup>-1</sup>	0.776 ± 0.023 (a)	- 0.854 ± 0.025 (b)		
$10^{29} \Delta\chi / J$ T <sup>-2</sup>	- 9.2 ± 0.7	- 16.2 ± 1.1		
$g_{\parallel}$	0.2468 ± 0.0004 (c)	0.067 ± 0.001 (d)		
$g_{\perp}$	0.00402 ± 0.00020 (c)	0.025 ± 0.002 (d)		
$10^{47}I_{\parallel} / \text{kg m}^2$	10.44 (e)	67.02 (d)		
$10^{47}I_{\perp} / \text{kg m}^2$	42.27 (e)	41.77 (d)		
(a) Reference 9	(b) Reference 10	(c) Reference 12	(d) Reference 5	(e) Reference 13

failure to exclude the contributions of the depolarized vibrational Raman scattering from the observed Rayleigh depolarization ratio.

The quadrupole moment for ethane is compared to previous results in Table 6.4. As expected there is only fair agreement between the results. The single-temperature field gradient birefringence measurement by Buckingham *et al.*,<sup>3</sup> which is really a measurement of  $\Theta + \frac{15BkT}{2\Delta\alpha}$ , is an overestimate, due to their assumption that the contribution of the hyperpolarizability term is negligible. However, when one compares the equivalent room-temperature measurement from this study,  $\Theta + \frac{15BkT}{2\Delta\alpha} = -(3.53 \pm 0.11) \times 10^{-40} \text{ C m}^2$ , with the result of Buckingham *et al.*, the agreement between the two quantities is excellent. This confirms that the magnitude of the first field gradient birefringence measurement of ethane by Buckingham *et al.*<sup>2</sup> was too low, even allowing for the different value of the polarizability anisotropy used in the calculation. The estimate obtained from the collision-induced far-infrared absorption study by Dagg *et al.*<sup>4</sup> is also in reasonable agreement with the present result, in which the two values overlap in the outer region of the uncertainty limits. The *ab initio* value is an overestimate of the quadrupole moment, due to the small basis set employed in the calculation.

In this study, several attempts were made to measure the field gradient birefringence effect in hexafluoroethane at room temperature and a gas pressure of  $\approx 900 \text{ kPa}$ ; however, no observable signal was able to be detected. A plausible explanation for such a result is that the sign of the quadrupole moment for hexafluoroethane is positive, opposite to that of ethane, as found for benzene and hexafluorobenzene. Assuming the quadrupole hyperpolarizability to be negative and the quadrupole moment to be positive, it would be possible for the temperature-independent and orientational terms to cancel each other out. This then provides some indication as to the magnitude of the quadrupole moment for hexafluoroethane. Given

TABLE 6.4 COMPARISON OF VALUES OF THE MOLECULAR QUADRUPOLE MOMENT OF ETHANE

Method	$10^{40}\Theta / \text{C m}^2$	Ref
field gradient birefringence, temperature dependence	$-2.25 \pm 0.15$	present work
field gradient birefringence, single temperature ( $B = 0$ )	$-3.40 \pm 0.13$	3
field gradient birefringence, single temperature ( $B = 0$ )	$-2.95 \pm 0.37$	2
collision-induced far i.r. absorption	$-2.37 - -4.27$	4
bond moment	$-3.00$	14
local multipole model	$-3.43$	15
SCF calculation	$-4.3$	6

that the hyperpolarizability of ethane is relatively small, one would expect the hyperpolarizability of hexafluoroethane to be of the same magnitude, thus the quadrupole moment of hexafluoroethane is estimated to be  $\Theta = 1.3 \pm 1.3 \times 10^{-40} \text{ C m}^2$ .

Also, an attempt was made to measure the field gradient birefringence effect in cyclohexane at temperatures between  $60^\circ\text{C}$  and  $100^\circ\text{C}$ , but, due to the low vapour pressures and the relatively small quadrupole moment, reliable results could not be obtained.

Previous estimates of the molecular quadrupole moment for cyclopropane are compared with the present result in Table 6.5. The estimate derived from the microwave Zeeman effect is in good agreement with the present value. The result was

obtained by studying the microwave spectrum of cyclopropane-HCl and cyclopropane-HCN complexes.<sup>5</sup> This enabled estimates of the magnetic anisotropy and molecular  $g$  values to be determined, which were then used to calculate the molecular quadrupole moment. As already mentioned, the single-temperature field gradient birefringence measurement by Buckingham *et al*<sup>3</sup> suffers from the assumption that the contribution of the quadrupole hyperpolarizability is negligible. Thus, their value of the quadrupole moment is overestimated again. Comparing their result to the room temperature result from this study,  $\Theta + \frac{15BkT}{2\Delta\alpha} = (7.95 \pm 0.22) \times 10^{-40} \text{ C m}^2$ , the agreement is rather poor and places some doubt on their result.

TABLE 6.5 COMPARISON OF VALUES OF THE MOLECULAR QUADRUPOLE MOMENT OF CYCLOPROPANE

Method	$10^{40}\Theta / \text{C m}^2$	Ref
field gradient birefringence, temperature dependence	$3.88 \pm 0.23$	present work
field gradient birefringence, single temperature ( $B = 0$ )	$5.7 \pm 0.8$	3
Zeeman effect	$3.5 \pm 1.3$	5
SCF calculation	8.4	7

Reported values of the magnetic anisotropies for ethane and cyclopropane are compared with the results from this work in Table 6.6. The values derived from this study were calculated using equation (1.45) and the parameters given in Table 6.3. For obvious reasons, the values of the magnetic anisotropy obtained from measurements of the temperature dependence of the Cotton-Mouton effect<sup>18</sup> are the most reliable.

The agreement amongst the values for ethane and cyclopropane, obtained from three different methods, is good and again demonstrates the reliability of the present values of the molecular quadrupole moments for these molecules.

TABLE 6.6 COMPARISON OF VALUES OF THE MAGNETIC ANISOTROPIES FOR ETHANE AND CYCLOPROPANE

Method	$C_2H_6$ ( $10^{29} \Delta\chi / J T^{-2}$ )	$C_3H_6$ ( $10^{29} \Delta\chi / J T^{-2}$ )
present work	$-9.2 \pm 0.7$	$-16.2 \pm 1.1$
Zeeman effect	$-9.7 \pm 0.7$ (a)	$-16.1 \pm 1.6$ (b)
magnetic birefringence, temperature dependence	$-10.0 \pm 0.4$ (c)	$-18.4 \pm 1.8$ (d)

(a) Reference 16

(b) Reference 5

(c) Reference 12

(d) Reference 17

This investigation of the temperature dependence of the field gradient birefringence effects of ethane and cyclopropane has shown that the contribution of the hyperpolarizability term to the observed effect, for molecules in this class, is very significant at normal temperatures. Thus, for weakly anisotropic molecules, the hyperpolarizability term must be separated from the orientational term in order to obtain reliable values for the molecular quadrupole moment. Although the observed effects for these molecules were much smaller than those produced from the other molecules studied in this project, the usefulness of this experiment as a means of obtaining reliable quadrupole moments and quadrupole hyperpolarizabilities, has again been demonstrated.

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## CHAPTER 7 – THE FIELD GRADIENT BIREFRINGENCE EFFECTS OF ACETYLENE, METHYLACETYLENE AND DIMETHYLACETYLENE

### 7.1 INTRODUCTION

Over the last 35 years, many experimental and theoretical methods for determining the molecular quadrupole moment have been applied to acetylene. These procedures, which include second virial coefficients,<sup>1</sup> the combination of the magnetic anisotropy (obtained from the microwave Zeeman effect or the Cotton-Mouton effect) with the molecular  $g$  value,<sup>2-4</sup> and collision-induced far-infrared absorption,<sup>5</sup> have yielded a wide range of values.

Of particular interest is a difference of 30% between two reported values of the quadrupole moment of acetylene, one by Kling *et al*<sup>2</sup> and the other by Coonan *et al*,<sup>4</sup> derived from independent investigations of the temperature dependence of the magneto-optical Cotton-Mouton effect. A theoretical calculation of the quadrupole moment of acetylene by Lindh and Liu,<sup>6</sup> with vibrational and correlational corrections, appears to indicate that the result of Coonan *et al* is the more reliable. Hence, one of the aims of this study was to remove any residual doubt as to the magnitude of the quadrupole moment of acetylene.

In contrast to the case of acetylene, very little information on the quadrupole moment of methylacetylene, and no information on the quadrupole moment of dimethylacetylene can be found in the literature.

As acetylene, methylacetylene and dimethylacetylene are small highly quadrupolar molecules, results from previous chapters and theoretical calculations suggest that the hyperpolarizability term will only make a small contribution to  ${}_mQ$  at room temperature for each of these molecules. Consequently, measurements of the field gradient induced birefringence were performed on these three compounds at a single temperature to obtain values of the quadrupole moments for acetylene, methylacetylene and dimethylacetylene. As methylacetylene possesses a permanent electric dipole moment, the derived quadrupole moment is reported relative to the effective quadrupole centre. The effective quadrupole moment is then combined with the centre of mass quadrupole moment of methylacetylene,<sup>7</sup> to estimate the position of the effective quadrupole centre.

## 7.2 EXPERIMENTAL

Samples used for measurements were as follows: acetylene (Matheson instrument grade, 99.5%, dissolved in acetone), passed through two traps in an ice-water-salt mixture to condense acetone vapour, purity >99.8%; methylacetylene (Matheson, purity >99.9%), used without purification; dimethylacetylene (Aldrich, purity >99%), subjected to three freeze-pump-thaw cycles prior to use, purity >99.6%. Each compound was analysed by gas chromatography.

Measurements on acetylene and methylacetylene were performed at 294 K, while measurements for dimethylacetylene were made at 300 K, at which temperatures reasonable vapour pressures were obtained. For acetylene, pressures were kept below 200 kPa, as above this pressure, at room temperature, the gas becomes unstable and potentially explosive. Published density virial coefficients<sup>8</sup> were used to calculate the number densities of acetylene and methylacetylene from the measured pressures. As no

density virial coefficients were available for dimethylacetylene, they were calculated from a Pitzer acentric analysis.<sup>9</sup>

The experimental results for acetylene, methylacetylene and dimethylacetylene are summarized in Tables 7.1, 7.2 and 7.3, respectively.

### 7.3 DISCUSSION

For a linear molecule, the general expression for the molar field gradient birefringence constant is given by

$${}_mQ = \frac{2N_A}{45\epsilon_0} \left\{ \frac{15}{2}B + \frac{1}{kT} \left[ \Theta\Delta\alpha - \frac{1}{2}\mu \left( 2a_1 + a_2 + 3a_3 + \frac{10}{\omega}G' \right) \right] \right\} \quad (7.1)$$

where  $a$  and  $G$  are higher polarizabilities. The  $z$ -axis is coincident with the symmetry axis of the molecule. For a dipolar molecule, the above expression gives the quadrupole moment relative to the effective quadrupole centre.

In previous chapters, measurements of the field gradient birefringence effect were performed over a range of temperatures to extract reliable values of the molecular quadrupole moment by separating the contribution of the temperature-independent term from the observed birefringence. However, for several reasons, this study of acetylene, methylacetylene and dimethylacetylene was limited to measurements of  ${}_mQ$  at a single temperature for each compound. Hence, in order to estimate the molecular quadrupole moments for these three molecules, it has been necessary to assume that the contribution of the hyperpolarizability term to the observed birefringence is negligible. To check whether or not this assumption was satisfactory, published theoretical values of the quadrupole hyperpolarizability for acetylene<sup>10,11</sup> were adjusted to provide an

TABLE 7.1 FIELD GRADIENT BIREFRINGENCE MEASUREMENTS ON  
ACETYLENE AT 294 K

Pressure / kPa	$10^8 E_{xx} / \text{V m}^{-2}$	$10^{26} \text{ }_m Q / \text{m}^5 \text{ V}^{-1} \text{ mol}^{-1}$
172.696	5.707	30.69
"	5.715	30.91
"	4.178	32.00
"	4.180	31.89
"	4.185	31.18
"	4.184	30.81
"	5.924	29.87
"	5.932	29.87
151.063	5.668	29.66
"	4.592	30.11
"	4.594	30.00
"	5.942	29.26
"	5.959	<u>29.34</u>
Mean = $30.4 \pm 0.9$		

TABLE 7.2 FIELD GRADIENT BIREFRINGENCE MEASUREMENTS ON  
METHYLACETYLENE AT 294 K

Pressure / kPa	$10^8 E_{xx} / \text{V m}^{-2}$	$10^{26} \text{ }_m Q / \text{m}^5 \text{ V}^{-1} \text{ mol}^{-1}$
296.598	3.801	50.78
"	3.797	51.37
"	3.537	50.81
"	3.537	51.57
283.910	3.759	51.93
"	3.759	51.84
"	3.991	51.87
299.509	3.816	51.48
"	3.816	51.06
"	3.816	51.15
"	3.346	51.20
"	3.346	51.45
"	4.015	50.98
"	4.015	<u>50.76</u>
		Mean = $51.3 \pm 0.4$

TABLE 7.3 FIELD GRADIENT BIREFRINGENCE MEASUREMENTS ON  
DIMETHYLACETYLENE AT 300 K

Pressure / kPa	$10^8 E_{xx} / \text{V m}^{-2}$	$10^{26} \rho_Q / \text{m}^5 \text{V}^{-1} \text{mol}^{-1}$
50.292	2.662	89.61
"	3.298	88.16
"	3.298	88.66
"	3.298	88.69
"	3.298	88.62
"	3.828	88.27
"	3.828	87.59
51.696	2.977	87.82
"	2.977	88.96
"	3.284	88.12
"	3.284	88.81
"	3.284	87.40
"	3.823	87.85
"	3.823	<u>89.12</u>
Mean = $88.4 \pm 0.6$		

experimental estimate of the quadrupole hyperpolarizability. This method involved comparing reported theoretical values of the hyperpolarizability for carbon dioxide and carbon disulfide by Amos,<sup>10</sup> and Maroulis and Thakkar<sup>12</sup> (for carbon dioxide), and Maroulis<sup>13</sup> (for carbon disulfide), with reliable experimental values (presented in Chapter 4) to derive a correction factor that could be applied to the theoretical results for acetylene. It was found that the calculations by Amos tended to underestimate the hyperpolarizability by a factor of 4, while the results of Maroulis, and Maroulis and Thakkar, overestimated the hyperpolarizability by  $\approx 33\%$ . By treating the results of Amos<sup>10</sup> and Maroulis and Thakkar<sup>11</sup> for acetylene in the appropriate manner, both yielded a value of  $B \approx -0.7 \times 10^{-60} \text{ C}^3 \text{ m}^4 \text{ J}^{-2}$ . At 294 K, this corresponds to a contribution of  $\approx -5\%$ . Consequently, the above assumption concerning the negligible contribution of the hyperpolarizability term is believed to be reasonable not only for acetylene but also for methylacetylene and dimethylacetylene, for the reason that methyl substitution is expected to have only a small effect on the magnitude of the hyperpolarizability. It should be emphasized that the foregoing is merely rationalization and serves only to provide an indication of the size of the contribution of the hyperpolarizability term to the birefringence for these species, so that reasonable estimates of the uncertainty in the derived quadrupole moments for these molecules can be made. An uncertainty of  $\pm 5\%$  has therefore been assigned to the values of the quadrupole moments for these molecules. Hence, for these relatively small but highly quadrupolar molecules, the large orientational term is expected to account for most of the observed birefringence.

The molecular quadrupole moments and polarizability anisotropies for acetylene, methylacetylene and dimethylacetylene, are given in Table 7.4. The polarizability anisotropies were derived from measurements of the depolarization ratios for Rayleigh scattered light at 632.8 nm.<sup>14,15</sup>

TABLE 7.4 MOLECULAR QUADRUPOLE MOMENTS AND POLARIZABILITY ANISOTROPIES OF ACETYLENE, METHYLACETYLENE AND DIMETHYLACETYLENE

Method	$10^{40}\Theta / \text{C m}^2$	$10^{40}\Delta\alpha / \text{C m}^2 \text{ V}^{-1}$
acetylene	$19.7 \pm 1.0$	$2.072 \pm 0.062$ (a)
methylacetylene	$18.4 \pm 0.9$	$3.75 \pm 0.11$ (a)
dimethylacetylene	$23.1 \pm 1.2$	$5.24 \pm 0.16$ (b)

(a) Reference 14

(b) Reference 15

A comparison of the present value of the quadrupole moment for acetylene with previous experimental and theoretical results is given in Table 7.5. As indicated in the table, many experimental methods have been used to determine the magnitude of the molecular quadrupole moment, resulting in a wide range of values. The present value is found to be in excellent agreement with the result of Coonan *et al.*,<sup>4</sup> who used measurements of the Cotton-Mouton effect to obtain the magnetic anisotropy of acetylene ( $\Delta\chi = -(3.94 \pm 0.25) \times 10^{-29} \text{ J T}^{-2}$ ) and combined this result with the known molecular  $g$  value to yield a value of the quadrupole moment. In addition, the best theoretical estimate,<sup>6</sup> calculated using large basis sets and corrected for correlational and vibrational effects, is in good agreement with the present direct experimental value. Apart from the result determined from collision-induced far-infrared absorption,<sup>5</sup> earlier estimates obtained from indirect methods such as second virial coefficients<sup>1</sup> are shown to be unreliable. From this comparison, it is clear that the investigation of the Cotton-Mouton effect of acetylene by Kling *et al.*<sup>2</sup> ( $\Delta\chi = -(6.25 \pm 0.16) \times 10^{-29} \text{ J T}^{-2}$ ) is unreliable.

TABLE 7.5 COMPARISON OF VALUES OF THE MOLECULAR QUADRUPOLE  
MOMENT FOR ACETYLENE

Method	$10^{40} \Theta / \text{C m}^2$	Ref
field gradient birefringence, single temperature	$19.7 \pm 1.0$	present work
Cotton-Mouton effect	$20.1 \pm 0.6$	4
Cotton-Mouton effect	$25.4 \pm 0.3$	2
microwave Zeeman effect	$26.7 \pm 5.3$	3
microwave Zeeman effect	$28.0 \pm 3.3$	16
collision-induced far i.r. absorption	$18.1 \pm 1.4$	5
X-ray diffraction	19.0 – 25.9	17
second virial coefficients	16.7	1
localized atom-dipole model	18.0	18
MP2 calculations	20.7	19
ACCD calculations	22.1	20
SDQ-MP4 calculations	21.9	21
MRSDCI-ANO calculations	$19.2 \pm 0.5$	6

As this is the first investigation of the field gradient birefringence effect of methylacetylene, the derived effective quadrupole moment, given in Table 7.4, cannot be directly compared to any previously reported results. However, a knowledge of both the effective quadrupole moment and the centre of mass quadrupole moment can be used to determine the position of the effective quadrupole centre. A value for the centre of mass quadrupole moment of methylacetylene, obtained from a study of the microwave Zeeman effect, has been reported by Shoemaker *et al.*<sup>7</sup> The centre of mass quadrupole moment is related to the effective quadrupole moment by equation (1.36). Combining the value of the centre of mass quadrupole moment reported by Shoemaker *et al.*,  $\Theta_{CM} = (16.1 \pm 0.8) \times 10^{-40} \text{ C m}^2$ , with the result for the effective quadrupole moment from this study, together with the known value of the dipole moment,<sup>22</sup>  $\mu = -(2.612 \pm 0.002) \times 10^{-30} \text{ C m}$ , the position of the effective quadrupole centre is found to lie 0.044 nm from the centre of mass in the  $-\text{C}\equiv\text{CH}$  direction.

The present result for the molecular quadrupole moment of dimethylacetylene, obtained from a single-temperature measurement of the field gradient birefringence, is the first experimentally determined value of the quadrupole moment. As the contribution from the temperature-independent term is expected to be negligible due to the large quadrupole moment of this relatively small molecule, this result is considered to be reliable.

The above investigation of the field gradient birefringence effects of acetylene, methylacetylene and dimethylacetylene has provided reliable estimates of the molecular quadrupole moments of these molecules. The present result for acetylene has removed any doubt surrounding the magnitude of the quadrupole moment and, consequently, the magnetic anisotropy of acetylene.

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## CHAPTER 8

## CONCLUSIONS

The most important conclusions that have resulted from the present work will be summarized in this chapter. With the significantly improved apparatus for measuring the temperature dependence of the field gradient birefringence effect, which was developed in this project, the full potential of the experiment as a means for determining reliable values of the quadrupole moment and quadrupole hyperpolarizability has been illustrated.

No pressure dependence of the molar field gradient birefringence constant was observed under the experimental conditions in this work for any of the compounds studied. Thus, the assumption that the molar field gradient birefringence constant is equal to the first field gradient birefringence virial coefficient, is valid. This is in contrast to the electrooptical Kerr effect where the second Kerr virial coefficients, which quantify contributions to the observed birefringence from interactions between pairs of molecules, are significant in many cases.<sup>1-4</sup>

In the present work, many challenges were encountered while performing measurements of the temperature dependence of the field gradient induced birefringence on these compounds. For benzene, hexafluorobenzene and carbon disulfide (compounds which are liquids at room temperature), low obtainable vapour pressures over the operating temperature range restricted the size of the applied electric field gradients and hence the observed birefringences. When a gas was studied, pressures were limited at the higher temperatures, due to the bending of the laser beam along the length of the quadrupole cell. As the size of the signal decreases when the temperature increases, this produces a larger uncertainty in the results at the higher temperatures. In particular, for nitrogen, ethane and cyclopropane, where the signal is already quite small due to the

small quadrupole moments of these molecules, measurements at the higher temperatures became very demanding.

At normal temperatures the orientational term dominated  ${}_mQ$  for all of the molecules studied except cyclopropane. From the analysis of the temperature dependence of  ${}_mQ$  in conjunction with the polarizability anisotropy, known from Rayleigh light scattering work, accurate values of the quadrupole moments were determined. In addition, reliable experimental values of the quadrupole hyperpolarizability were obtained in most cases, despite the long extrapolation required in the derivation. With the exception of carbon dioxide, where a previous estimate of the hyperpolarizability has been reported,<sup>5</sup> these values of the hyperpolarizability provide the first reliable information on this quantity for these molecules.

Table 8.1 summarizes the values of the quadrupole hyperpolarizability for these molecules, and the relative contributions they make to  ${}_mQ$  at 300 K. It can be seen that the magnitude of the hyperpolarizability generally increases as the size of the molecule increases, so that the smaller aliphatic molecules like ethane have a hyperpolarizability an order of magnitude smaller than the larger aromatic molecules. Also, the hyperpolarizability contributions to  ${}_mQ$  at normal temperatures are relatively small for the highly anisotropic molecules, but become much more significant for the weakly anisotropic species. As a result of this, reliable values of the quadrupole moment for highly anisotropic molecules may be obtained from single-temperature measurements of the field gradient birefringence effect, as was the case for acetylene, methylacetylene and dimethylacetylene. However, for species such as ethane and cyclopropane that have small quadrupole moments, it has been shown that it is essential to remove the contribution of the hyperpolarizability term, otherwise the derived quadrupole moment may be seriously in error.

TABLE 8.1 QUADRUPOLE HYPERPOLARIZABILITIES AND THEIR RELATIVE CONTRIBUTIONS TO  ${}_mQ$  AT 300 K

Molecule	$10^{60}B / C^3 \text{ m}^4 \text{ J}^{-2}$	% Contribution
Carbon dioxide	$- 0.27 \pm 0.13$	$2.4 \pm 1.2$
Carbon disulfide	$- 2.0 \pm 1.3$	$- 5.4 \pm 3.5$
Benzene	$- 5.1 \pm 0.7$	$- 9.1 \pm 1.3$
Hexafluorobenzene	$- 4.9 \pm 3.4$	$7 \pm 5$
Ethane	$- 0.33 \pm 0.04$	$37 \pm 5$
Cyclopropane	$- 1.15 \pm 0.05$	$52 \pm 3$
Nitrogen	$- 0.14 \pm 0.03$	$9.9 \pm 2.6$

The results from this study have removed any doubt surrounding the magnitude of the quadrupole moment that had arisen for several molecules due to the inconsistent values reported in the literature. These include carbon dioxide and acetylene, where published values were found to differ by as much as 30%. Also, much important information on the molecular quadrupole moment has been obtained from the series of molecules studied. In particular, the effect of atom substitution on the sign and magnitude of the quadrupole moment in related molecules, such as carbon dioxide and carbon disulfide, and benzene and hexafluorobenzene, has been investigated.

For dipolar molecules, quadrupole moments determined from measurements of the field gradient induced birefringence are defined relative to the effective quadrupole centre. From the effective quadrupole moments of methylacetylene (chapter 7) and

carbonyl sulfide (chapter 4) it was possible to determine the position of the effective quadrupole centres of both of these molecules (using the relationship between the effective quadrupole moment and the centre of mass quadrupole moment).

In the foregoing chapters, comparisons made between the present values of the quadrupole moment and previously reported results, obtained from various methods, have shown that the most reliable experimental values have come from collision-induced far-infrared absorption studies or by combining the magnetic anisotropy with the molecular  $g$  value, to calculate the quadrupole moment. Also, theoretical calculations, performed using large basis sets, have yielded results in good agreement with the present values.

For several molecules discussed in this work, present values of the quadrupole moment have been used to calculate the magnetic anisotropy using known values of the molecular  $g$  value and moments of inertia. These derived magnetic anisotropies showed good agreement with the best published values obtained from Cotton-Mouton effect studies or the microwave Zeeman effect.

This study has shown that the temperature dependence of the field gradient birefringence effect of molecules in the gas phase is an extremely powerful technique for the determination of the molecular quadrupole moment and the quadrupole hyperpolarizability. With a notable lack of reliable experimental values of the quadrupole moment available, it is hoped that the present apparatus will provide the opportunity for many other studies.

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## APPENDIX 1 – TEMPERATURE DEPENDENCE OF THE FIELD GRADIENT BIREFRINGENCE EFFECT OF NITROGEN

### A1.1 INTRODUCTION

The molecular quadrupole moment of nitrogen has been the object of much study. Many experimental and theoretical values have been reported over the years, and values can be found in the literature as early as 1954.<sup>1</sup> Several indirect methods that have been used to estimate the quadrupole moment include collision-induced far-infrared absorption,<sup>2,3</sup> ion-molecule scattering<sup>4</sup> and microwave line broadening.<sup>5,6</sup> In addition, results have been obtained using the direct method of the field gradient birefringence experiment, but these values suffer from the doubtful assumption that the contribution of the hyperpolarizability term to the observed birefringence is zero.<sup>7-10</sup> Thus, despite all of these results, it is apparent that there is still no agreed value of the molecular quadrupole moment of nitrogen.

More recently, several theoretical calculations, employing large basis sets, have been performed to determine the molecular quadrupole moment of nitrogen.<sup>11-13</sup> As nitrogen is a small molecule of high symmetry, the theoretically derived quadrupole moments are expected to be quite reliable. The agreement shown between the theoretical values and some of the experimental values appears to confirm this prediction.

However, to remove any uncertainty as to the true magnitude of the molecular quadrupole moment, the temperature dependence of the field gradient birefringence

effect of nitrogen was measured. The results from this study enabled a comparison to be made with other field gradient birefringence measurements that were performed by other workers at single temperatures. In addition, this study provides the first experimentally derived value of the quadrupole hyperpolarizability of nitrogen.

### A1.2 EXPERIMENTAL

Nitrogen (CIG ultra high-purity >99.99%) was used without purification. Measurements of the field gradient birefringence were made at eight temperatures (293 - 412 K). Recorded density virial coefficients<sup>14</sup> were used to calculate values of the gas density from the observed pressures. An analysis of the sample using gas chromatography showed that there were no significant impurities.

The experimental results are summarized in Table A1.1.

### A1.3 DISCUSSION

The temperature dependence of the molar field gradient birefringence constant for a linear non-dipolar molecule is given by

$${}_mQ = \frac{2N_A}{45\epsilon_0} \left\{ \frac{15}{2} B + \frac{\Delta\alpha\Theta}{kT} \right\} \quad (\text{A1.1})$$

Figure A1.1, constructed from the data in Table A1.1, illustrates the linear dependence of  ${}_mQ$  on  $T^{-1}$ . The analysis of the experimental data and the derived molecular properties are presented in Table A1.2.

TABLE A1.1 FIELD GRADIENT BIREFRINGENCE EFFECT OF NITROGEN AT 632.8 nm

$T / \text{K}$	No. Runs	$p_{\text{max}} / \text{kPa}$	$10^6 B / \text{m}^3 \text{mol}^{-1(\text{a})}$	No. Measurements	$10^{26} {}_m Q / \text{m}^5 \text{V}^{-1} \text{mol}^{-1}$
293.2	6	1774.8	-5.84	60	$-3.17 \pm 0.03$
311.2	6	1872.3	-2.50	60	$-3.00 \pm 0.04$
327.2	8	2011.7	0.45	80	$-2.84 \pm 0.05$
347.2	6	1332.8	3.60	60	$-2.74 \pm 0.07$
365.2	6	1349.5	5.72	60	$-2.56 \pm 0.07$
378.2	6	1380.8	7.37	60	$-2.56 \pm 0.08$
395.2	6	1342.3	9.04	72	$-2.44 \pm 0.09$
412.2	7	1335.1	10.54	84	$-2.35 \pm 0.11$

(a) Reference 14

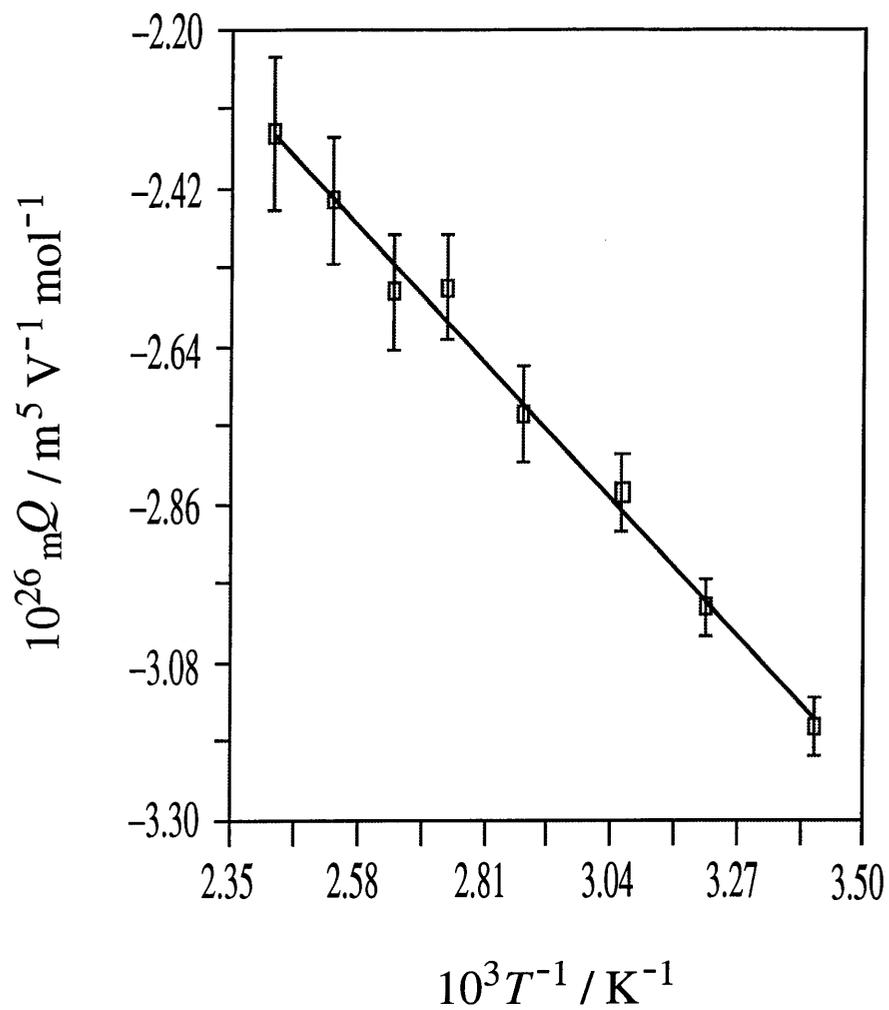


Figure A1.1 Temperature dependence of the field gradient birefringence effect of nitrogen.

TABLE A1.2 ANALYSIS OF THE FIELD GRADIENT BIREFRINGENCE  
EFFECT OF NITROGEN

Property	Value
$10^{26}$ intercept / $m^5 V^{-1} mol^{-1}$	$- 0.305 \pm 0.077$
$10^{23}$ slope / $m^5 V^{-1} K mol^{-1}$	$- 0.839 \pm 0.025$
$10^{60}B / C^3 m^4 J^{-2}$	$- 0.135 \pm 0.034$
$10^{40}\Theta / C m^2$	$- 4.89 \pm 0.19$
$10^{40}\Delta\alpha / C^2 m^2 J^{-1}$ (a)	$0.783 \pm 0.023$

(a) Reference 15

The quadrupole hyperpolarizability derived from this study,  $B = - (0.135 \pm 0.034) \times 10^{-60} C^3 m^4 J^{-2}$ , is in fair agreement with the theoretical estimate,  $B = - 0.25 \times 10^{-60} C^3 m^4 J^{-2}$ , obtained from SDQ-MBPT calculations by Maroulis.<sup>12</sup> At 300 K, the relative contribution of the hyperpolarizability term to  ${}_mQ$  is  $(9.9 \pm 2.6)\%$ .

Previous experimental and theoretical estimates of the molecular quadrupole moment of nitrogen are compared with the present result in Table A1.3. Although not obvious from Table A1.3, all of the previous results obtained from measurements of the field gradient birefringence are too low when compared with the present value, despite the fact that the values appear to be in good agreement. This study has shown that the hyperpolarizability term contributes a significant 10% to the observed birefringence, but as all of the single-temperature measurements assume  $B = 0$ , the magnitude of the quadrupole moment is overestimated in each case. As expected, the agreement between the theoretical values and the present result is excellent, thus confirming the magnitude

TABLE A1.3 COMPARISON OF VALUES OF THE MOLECULAR QUADRUPOLE  
MOMENT OF NITROGEN

Method	$10^{40}\Theta / \text{C m}^2$	Ref
field gradient birefringence, temperature dependence	$-4.89 \pm 0.19$	present work
field gradient birefringence, single temperature ( $B = 0$ )	$-4.72 \pm 0.26$	7
field gradient birefringence, single temperature ( $B = 0$ )	$-4.90 \pm 0.3$	8
field gradient birefringence, single temperature ( $B = 0$ )	$-4.67 \pm 0.3$	9
field gradient birefringence, single temperature ( $B = 0$ )	$-5.07 \pm 0.3$	10
second virial coefficient	$-4.90 \pm 0.23$	16
collision-induced far i.r. absorption	$-5.00 \pm 0.33$	2
collision-induced far i.r. absorption	$-5.04$	3
ion-molecule scattering	$-5.00 \pm 1.7$	4
MBPT calculation	$-4.97 \pm 0.17$	11
MBPT calculation	$-4.99$	12
MBPT calculation	$-5.10$	13

of the molecular quadrupole moment of nitrogen. In addition, the estimates of the molecular quadrupole moment obtained from collision-induced far-infrared absorption studies are in good agreement with the present result, once again demonstrating the effectiveness of this procedure for determining molecular quadrupole moments.

From the analysis of the temperature dependence of the field gradient birefringence effect of nitrogen, the magnitude of the molecular quadrupole moment of this species can now be considered beyond doubt. Also, a reliable value of the quadrupole hyperpolarizability has been determined, thus providing additional important information about this molecule.

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