APPENDIX I - THE PRINCIPAL POLARIZABILITIES
OF PYRIDINE

AI.1 INTRODUCTION

The gas-phase principal polarizabilities of pyridine have previously been determined using the combination of a single-temperature Kerr constant, the mean polarizability and the Rayleigh depolarization ratio.[1] However, the derived values are somewhat unreliable due to the use of data obtained at different optical frequencies and also because of various assumptions made about electric hyperpolarizabilities. Solution-phase Kerr effect measurements[2] of pyridine as a solute in cyclohexane have provided polarizabilities that are unlikely to be appropriate to the free-molecule state. Clearly, it was of interest to obtain reliable values of these properties. In the present work, it has proved possible to determine the free-molecule polarizabilities from a study of the temperature dependence of the Cotton-Mouton effect of pyridine, for which the results are presented in this section, in combination with the Rayleigh depolarization ratio obtained at $\lambda = 632.8$ nm,[3] the mean polarizability[4] and the magnetizabilities derived from a Zeeman effect study.[5]

AI.2 EXPERIMENTAL RESULTS

Pyridine (Merck, >99.5%) was fractionally distilled from phosphorus pentoxide and subjected to two freeze-pump-thaw cycles in the vapour-handling system prior to measurements. Gas-chromatographic analysis indicated a purity of at least 99.8%. The magnetic field-induced birefringence at $\lambda = 632.8$ nm was measured at 10 temperatures in the range 293-447 K and, at each temperature, at several

pressures up to approximately 75% of the equilibrium vapour pressure. The low pressures, particularly at room temperature, and the diminution of the effect at higher temperatures, limited the range of the measurements in comparison with other studies.

Gas densities were calculated from measured gas pressures and temperatures using published density second virial coefficients.[6] The results of measurements are summarized in Table AI.1, where the uncertainties shown are based on the standard deviations derived from least-squares straight lines.

AI.3 ANALYSIS AND DISCUSSION

The molecular axes are defined to be such that the x-axis is coincident with the C_2 axis, the ring lies in the xy-plane and the z-axis is perpendicular to the ring. The relevant equations describing the molecular parameters in the Rayleigh depolarization ratio, the mean polarizability, and the combination of polarizability and magnetizability tensors derived from the present Cotton-Mouton effect study are as follows:

$$5\rho_0(3-4\rho_0)^{-1} = \kappa^2$$

$$= \left[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 \right] / 18\alpha^2 \qquad \text{(AI.1)}$$

$$(2V_m\varepsilon_0/N_A)(n-1) = \alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \qquad \text{(AI.2)}$$

$$_mC = \left(\frac{N_A\mu_0{}^2}{270\varepsilon_0} \right) \left\{ \Delta\eta + \frac{1}{kT} \left[\alpha_{xx}(\chi_{xx} - \chi) + \alpha_{yy}(\chi_{yy} - \chi) + \alpha_{zz}(\chi_{zz} - \chi) \right] \right\} \qquad \text{(AI.3)}$$

The linear dependence of $_mC$ on T^{-1} predicted by equation (AI.3) was observed and

TABLE AI.1   COTTON-MOUTON EFFECT OF PYRIDINE AT $\lambda = 632.8$ nm

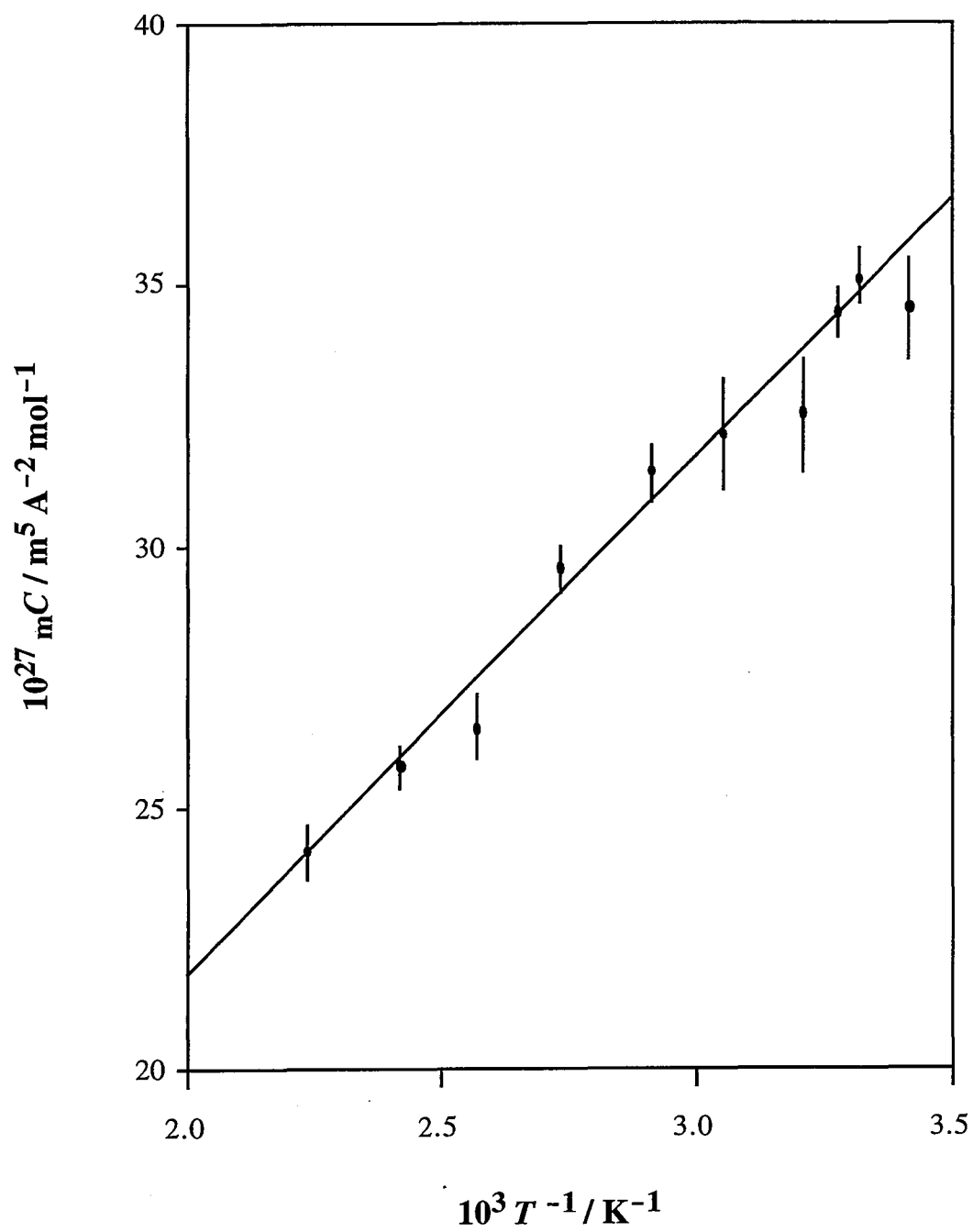| T / K	No. of pressures	Maximum p / kPa	$10^6 B$ / m^3mol^{-1}	$10^{27}{}_mC$ / $m^5A^{-2}mol^{-1}$
447.4	9	5.9	−650	24.15 ± 0.50
413.4	8	6.6	−800	25.75 ± 0.40
389.1	12	8.6	−940	26.53 ± 0.60
365.9	11	9.3	−1125	29.52 ± 0.43
343.6	11	8.3	−1370	31.38 ± 0.50
327.7	9	5.0	−1600	32.11 ± 1.06
311.8	10	4.1	−1890	32.52 ± 1.08
305.1	12	3.1	−2050	34.48 ± 0.48
301.3	8	1.8	−2145	35.12 ± 0.48
292.6	8	1.7	−2385	34.55 ± 0.94

Figure AI.1   Temperature dependence of the vapour-state Cotton-Mouton effect of pyridine.

is shown in Figure AI.1, and the intercept and slope of the least-squares straight line are in Table AI.2. The simultaneous solution of the above equations, using the data in Table AI.2, yielded the polarizability components shown in Table AI.2. Two possible sets of the polarizabilities result, due to the quadratic dependence of ρ_0 on the polarizability tensor, evident from equation (AI.1). Values of each polarizability component in both sets were calculated by varying each parameter within its error, and the uncertainty of each value was taken to be the difference between the solution and the most deviant value obtained; for these reasons, it is believed that the uncertainties are somewhat overestimated. In an attempt to determine which set of polarizabilities is the correct one for pyridine, the present results were compared with values obtained from other experimental and theoretical studies, summarized in Table AI.3.

The previous gas-phase polarizabilities[1] were determined by combination of a single-temperature Kerr constant using white light, in conjunction with the mean polarizability and the Rayleigh depolarization ratio at $\lambda = 488.0$ nm. In addition, a value of β^K was calculated from second harmonic generation data using an assumed value of γ^K;[7] however, the relative contributions of β^K and γ^K to the Kerr constant are only 1.5% and 2.0%, respectively, and therefore almost negligible. Although the derived polarizabilities were unreliable due to the combination of data obtained at different wavelengths, it was of interest to compare these with the present values. It is apparent that neither set of polarizabilities in Table AI.2 agrees with those determined by Burnham and Gierke; however, it is worthy of note that the relationship observed, $\alpha_{yy} > \alpha_{xx} > \alpha_{zz}$, is in agreement with the values in Set Two in Table AI.2.

A study[2] of the solution-phase Kerr effect of pyridine as a solute in cyclohexane at $\lambda = 632.8$ nm was used in conjunction with the molar refraction to obtain the out-of-plane component, α_{zz}, of the polarizability. In the analysis, it was assumed that the two in-plane components are equivalent, so that it was not possible

TABLE AI.2 ANALYSIS OF THE TEMPERATURE DEPENDENCE OF THE COTTON-MOUTON EFFECT OF PYRIDINE AT $\lambda = 632.8$ nm

Property	Value	
10^{27}intercept / $m^5A^{-2}mol^{-1}$	1.8 ± 1.3	
10^{24}slope / $m^5A^{-2}K\,mol^{-1}$	9.96 ± 0.46	
$10^{50}\Delta\eta$ / $C\,m^2V^{-1}T^{-2}$	500 ± 300	
$10^{43}\left[\alpha_{xx}(\chi_{xx}-\chi)+\alpha_{yy}(\chi_{yy}-\chi)+\alpha_{zz}(\chi_{zz}-\chi)\right]$ / $C^2m^2T^{-2}mol^{-1}$	2.081 ± 0.096	
$10^5(2\chi_{xx}-\chi_{yy}-\chi_{zz})$ / $J\,T^{-2}mol^{-1}$ [a]	54.3 ± 0.6	
$10^5(2\chi_{yy}-\chi_{xx}-\chi_{zz})$ / $J\,T^{-2}mol^{-1}$ [a]	60.5 ± 0.8	
$10^{29}\chi$ / $J\,T^{-2}$ [b]	-81.0 ± 1.0	
$10^2\rho_0$ [c]	2.05 ± 0.04	
$10^{40}\alpha$ / $C\,m^2\,V^{-1}$ [d]	10.56 ± 0.04	
	Set One	Set Two
$10^{40}\alpha_{xx}$ / $C\,m^2V^{-1}$	13.7 ± 1.0	10.9 ± 1.6
$10^{40}\alpha_{yy}$ / $C\,m^2V^{-1}$	11.1 ± 1.7	13.8 ± 1.2
$10^{40}\alpha_{zz}$ / $C\,m^2V^{-1}$	6.9 ± 0.9	7.0 ± 1.0

[a] Reference 5. [b] Reference 8.

[c] Reference 3. [d] Reference 4.

TABLE AI.3 VALUES OF THE MOLECULAR POLARIZABILITY COMPONENTS [a] OF PYRIDINE

Year	Method	α_{xx}	α_{yy}	α_{zz}	Ref.
1977	Solution-phase Kerr constant and α, assumed $\alpha_{xx} = \alpha_{yy}$	12.0	12.0	7.8	2
1979	SCF calculations (zero-frequency values)	12.02	12.24	6.89	9
1980	Single-temperature Kerr constant, α and ρ_0 (see text)	12.26	13.28	6.91	1
1990	SCF calculations (scaled to $\lambda = 632.8$ nm)	12.23	13.02	6.57	10b
1994	SDQ-MP4 calculations (with MP2 corrections) (zero-frequency values)	11.99	12.71	6.77	11
1994	Temperature dependence of Kerr effect, μ, ρ_0 and α	12.19 ± 0.17	12.83 ± 0.29	6.63 ± 0.09	12
1994	Temperature dependence of Cotton-Mouton effect, χ, ρ_0 and α; two sets of values result: Set One	13.7 ± 1.0	11.1 ± 1.7	6.9 ± 0.9	
	Set Two	10.9 ± 1.6	13.8 ± 1.2	7.0 ± 1.0	

[a] Expressed in units of $\times 10^{-40}$ $C\,m^2V^{-1}$. All values at $\lambda = 632.8$ nm, unless otherwise indicated.

Appendix 1 Pyridine

to use this information to decide which of the two sets of polarizability components shown in Table AI.2 is correct.

As shown in Chapter 5 for dimethyl ether and related molecules, scaled theoretical calculations[10a] by Spackman are in excellent agreement with experimentally determined polarizabilities. However, this is not the case for pyridine, but the relationship $\alpha_{yy} > \alpha_{xx} > \alpha_{zz}$ is observed for all three sets of theoretical results shown in Table AI.3.

Recently, a study of the temperature dependence of the Kerr effect of pyridine[12] was completed, and the analysis, in combination with the dipole moment, the Rayleigh depolarization ratio and the mean polarizability yielded a unique set of polarizabilities, shown in Table AI.3, in contrast to the analysis using the data from the Cotton-Mouton effect. As noted above, these values do not agree closely with either set of the polarizability components shown in Table AI.2 but the relationship $\alpha_{yy} > \alpha_{xx} > \alpha_{zz}$ is again apparent.

From the polarizabilities determined in the two experimental studies and estimated from theoretical calculations, it is believed that the choice of polarizability components labelled Set Two in Table AI.2 is correct, as the relationship $\alpha_{yy} > \alpha_{xx} > \alpha_{zz}$ is observed in all cases. Furthermore, the value of α_{xx} of Set One is in complete disagreement with values of α_{xx} determined by other techniques, even when experimental uncertainties are taken into account. However, the errors in the magnetizability components and in the combination of the polarizability and magnetizability tensors determined from the Cotton-Mouton effect have introduced a relatively high uncertainty into each of the polarizability components. The limitations of low attainable pressures and lack of adequate precision in the necessary data have resulted in values of the polarizabilities that are as good as could possibly expected in this study.

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APPENDIX II - THE PRINCIPAL POLARIZABILITIES
OF ETHYLENE

AII.1 INTRODUCTION

The gas-phase principal polarizability components of ethylene have recently been derived[1] from an analysis of the temperature dependence of the Kerr effect together with results from a previous study of the temperature dependence of the Cotton-Mouton effect,[2] the mean polarizability[3] and the magnetizabilities obtained from the microwave Zeeman effect study of the deuterated species.[4] As shown in previous chapters, there were serious differences in results obtained for ethane and acetylene between this and previous Cotton-Mouton effect studies, and it was therefore considered appropriate to re-examine the effect in ethylene. The free-molecule polarizabilities of ethylene were obtained from an analysis of the temperature dependence of the Cotton-Mouton effect, for which the results of measurements are presented here, in combination with the polarizability tensor component ratio, R_{20},[5] the mean polarizability and the magnetizabilities derived from the microwave Zeeman effect study.

AII.2 EXPERIMENTAL RESULTS

The sample of ethylene (Matheson, chemically pure), used without further purification, was analyzed by gas chromatography to confirm the purity as $> 99.5\%$. Measurements of the magnetic-field induced birefringence at $\lambda = 632.8$ nm were conducted at 8 temperatures in the range 293-438 K and, at each temperature, over a range of pressure (up to 900 kPa). Gas densities were calculated from measured gas

TABLE AII.1   COTTON-MOUTON EFFECT OF ETHYLENE AT $\lambda = 632.8$ nm

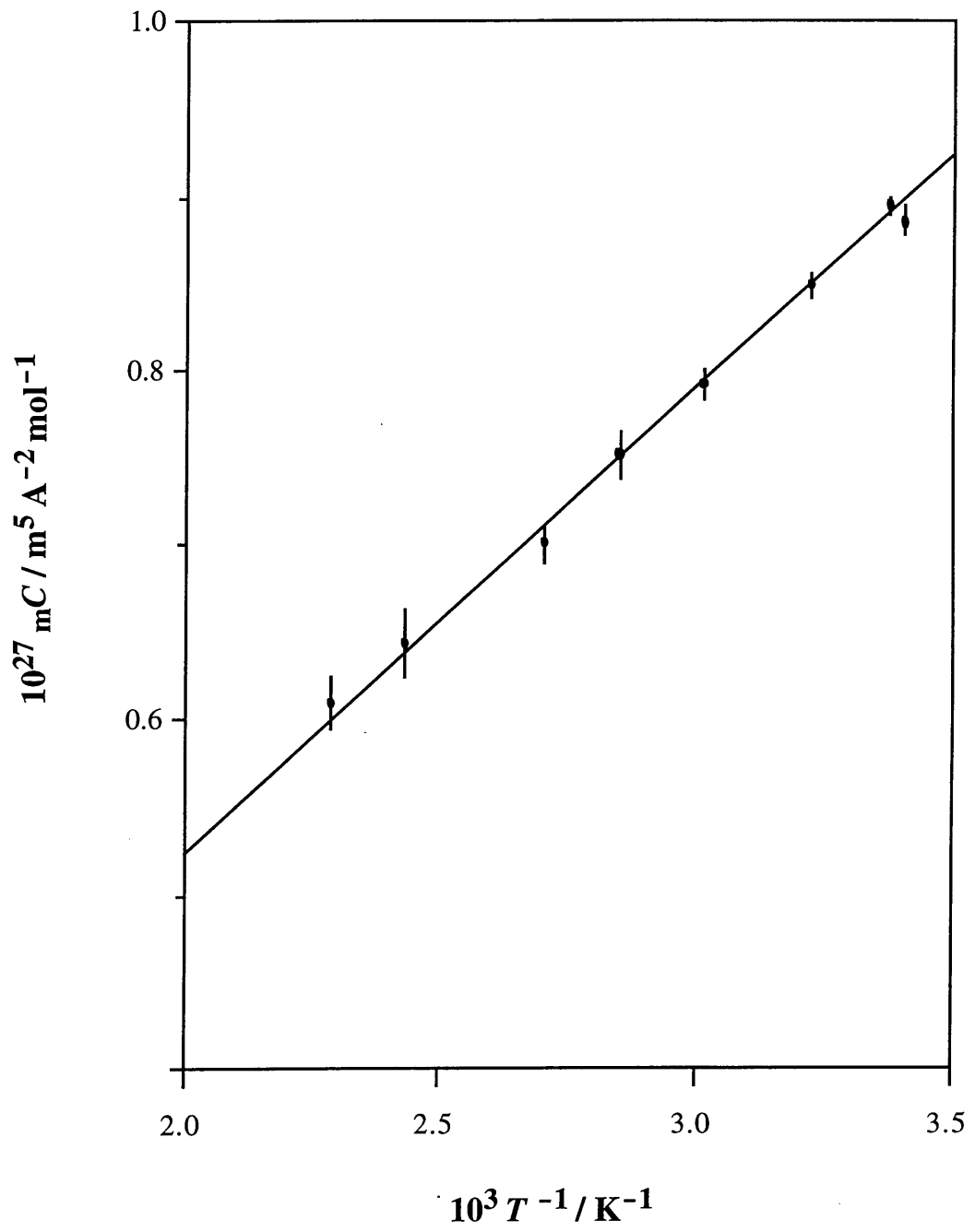| T / K	No. of pressures	Maximum p / kPa	$10^6 B$ / $m^3 mol^{-1}$	$10^{27}{}_m C$ / $m^5 A^{-2} mol^{-1}$
437.9	10	250	−56	0.609 ± 0.015
411.4	16	250	−66	0.644 ± 0.019
369.8	8	493	−86	0.701 ± 0.011
351.1	9	450	−98	0.751 ± 0.013
331.1	8	599	−112	0.791 ± 0.009
310.4	8	600	−130	0.848 ± 0.007
296.5	11	935	−144	0.895 ± 0.005
293.5	8	631	−147	0.885 ± 0.009

Figure AII.1 Temperature dependence of the Cotton-Mouton effect of ethylene.

TABLE AII.2 ANALYSIS OF THE TEMPERATURE DEPENDENCE OF THE COTTON-MOUTON EFFECT OF ETHYLENE AT $\lambda = 632.8$ nm

Property	Value	Literature value
10^{27} intercept / $m^5A^{-2}mol^{-1}$	-0.009 ± 0.029	
10^{24} slope / $m^5A^{-2}K\,mol^{-1}$	0.2663 ± 0.0092	
$10^{50}\Delta\eta$ / $C\,m^2V^{-1}T^{-2}$	-2 ± 7	-0.3 ± 0.9 [a]
$10^{45}\left[\alpha_{xx}(\chi_{xx} - \chi) + \alpha_{yy}(\chi_{yy} - \chi) + \alpha_{zz}(\chi_{zz} - \chi)\right]$ / $C^2m^2T^{-2}mol^{-1}$	5.57 ± 0.19	5.68 ± 0.27 [a]
$10^5\left(2\chi_{zz} - \chi_{xx} - \chi_{yy}\right)$ / $J\,T^{-2}mol^{-1}$ [b]	4.57 ± 0.13	
$10^5\left(2\chi_{xx} - \chi_{yy} - \chi_{zz}\right)$ / $J\,T^{-2}mol^{-1}$ [b]	11.60 ± 0.27	
$10^{29}\chi$ / $J\,T^{-2}$ [c]	-33.4 ± 1.0	
R_{20} [d]	0.31 ± 0.04	
$10^{40}\alpha$ / $C\,m^2\,V^{-1}$ [e]	4.7124 ± 0.0005	
$10^{40}\alpha_{xx}$ / $C\,m^2V^{-1}$	4.29 ± 0.15	
$10^{40}\alpha_{yy}$ / $C\,m^2V^{-1}$	3.76 ± 0.25	
$10^{40}\alpha_{zz}$ / $C\,m^2V^{-1}$	6.09 ± 0.20	

[a] Reference 2.   [b] Reference 4.

[c] Reference 7.   [d] Reference 5.

[e] Reference 3.

TABLE AII.3 VALUES OF THE MOLECULAR POLARIZABILITY COMPONENTS [a] OF ETHYLENE

Year	Method	α_{xx}	α_{yy}	α_{zz}	Ref.
1975	R_{20}, α and ρ_0 (recalculated values, see text; $\lambda = 514.5$ nm)	4.37	3.86	6.14	5
1985	SCF calculations (zero-frequency values; results confirmed by a subsequent study)	4.06	3.79	6.05	10, 11
1988	Stark effect (static values)	4.06	3.98	6.15	14
1989	MP2 calculations (zero-frequency values)	4.09	3.53	5.59	12
1992	SDQ-MP4 calculations (zero-frequency values)	4.14	3.66	5.63	13
1994	Temperature dependence of the Kerr and Cotton-Mouton effects,,χ, α and $\alpha_{\alpha\beta}^0$	4.62 ± 0.07	3.86 ± 0.04	5.66 ± 0.08	1
1994	Temperature dependence of the Cotton-Mouton effect, χ, R_{20} and α	4.29 ± 0.15	3.76 ± 0.25	6.09 ± 0.20	

[a] Expressed in units of $\times 10^{-40}$ $C\,m^2V^{-1}$. All values at $\lambda = 632.8$ nm, unless otherwise indicated.

There have been numerous reports of ab initio values of the polarizabilities,[10-13] as evident in Table AII.3, and, in each case, the relationship $\alpha_{zz} > \alpha_{xx} > \alpha_{yy}$ was found. The results from SDQ-MP4 calculations,[13] which include electron correlation effects, are expected to be the most accurate theoretical values currently available. However, it should be borne in mind that these methods yield zero-frequency polarizabilities, and allowances must be made for electronic contributions when comparing them with optical-frequency values.

The present information offers an opportunity for comparison with values determined from the Stark effect[14] and the most recent ab initio results.[13] Polarizability components derived from the Stark effect are static values, that is, they contain vibrational contributions, which can readily be estimated from integrated infrared intensities. A further difference between static and optical-frequency values is the dispersion in the electronic component, and, as discussed previously, a linear dependence on ω^2 is expected, provided the electronic states are well removed from optical frequencies.[15] The polarizabilities determined from various experimental methods and the most recent ab initio value are shown in Figure AII.2, with the straight lines representing the lines of best fit through values derived from the present work (at $\lambda = 632.8$ nm), from Hills and Jones[5] (at $\lambda = 514.5$ nm) and from Maroulis[13] ($\omega = 0$). The linear relationship expected for each polarizability component is apparent in Figure AII.2, although the uncertainties are not shown. Using integrated infrared intensity data,[16] it was possible to estimate vibrational contributions to the polarizability, which are shown in Table AII.4. It is obvious that subtracting these contributions from the static values determined by Chen and Oka result in zero-frequency values which are in poor agreement with the most recent ab initio results. The agreement of α^0 obtained by Bose and Cole[17] with the vibrational contribution added to the pure electronic static value, $\alpha^0_{el} = 4.584 \times 10^{-40} C\, m^2 V^{-1}$,[3] is excellent, and indicates the reliability of the integrated infrared intensity data. The
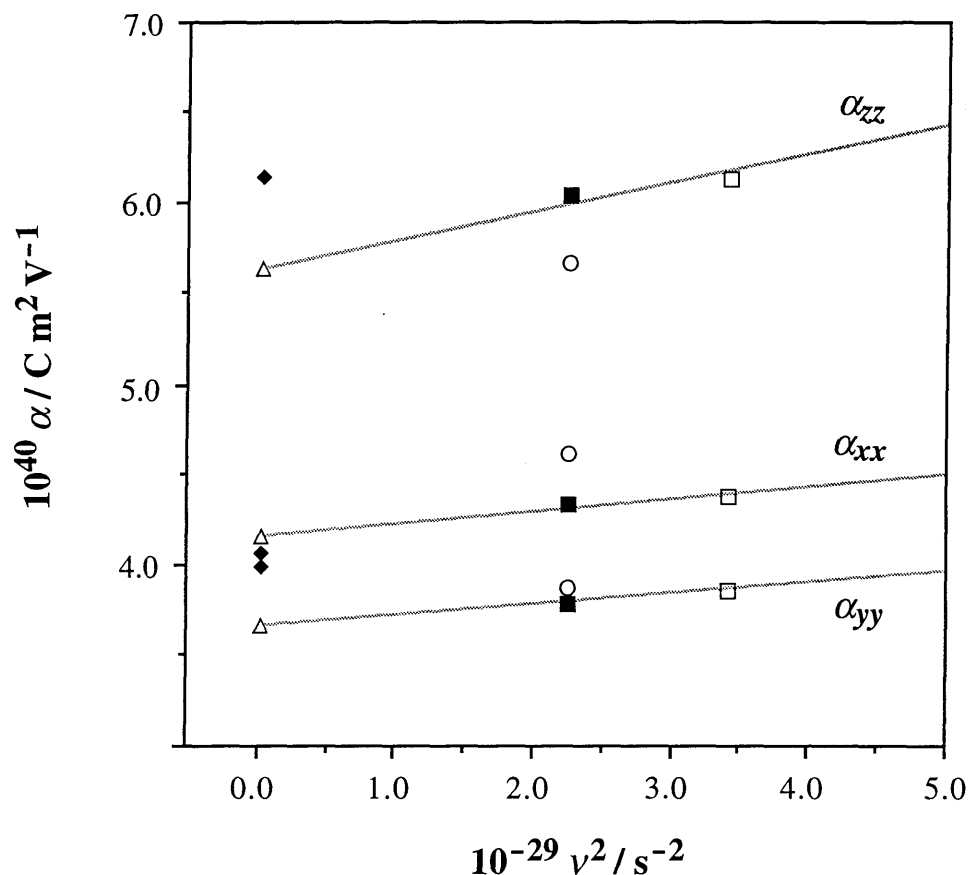
Figure AII.2 Frequency dependence of the polarizability components of ethylene.

■, present work; □, reference 5, revised values (see text); o, reference 1; △, reference 13; ◆, reference 14.

static polarizability anisotropies determined from the Stark effect[14] are somewhat imprecise,

$$\alpha^0_{zz} - \left(\alpha^0_{xx} + \alpha^0_{yy}\right)/2 = (2.13 \pm 0.15) \times 10^{-40} \text{ C m}^2 \text{ V}^{-1}$$

$$\alpha^0_{xx} - \alpha^0_{yy} = (0.08 \pm 0.15) \times 10^{-40} \text{ C m}^2 \text{ V}^{-1}$$

and it seems possible that more reliable values of the static polarizabilities can be

obtained using ab initio results and vibrational contributions, as shown in Table AII.4. The Stark shift, from which the above anisotropies were determined, was complicated by a second-order Stark effect due to the near degeneracy of the v_7 and v_8 vibrational states, and a perturbation technique was used to account for the effect;[14] any possible deficiency in the correction may lead to significant variations in the values obtained.

TABLE AII.4   COMPARISON OF EXPERIMENTAL AND ESTIMATED STATIC POLARIZABILITIES OF ETHYLENE

	α_{xx}	α_{yy}	α_{zz}	Ref.
$10^{40}\alpha^0_{vib}$ / $C\,m^2\,V^{-1}$	0.011	0.401	0.033	16
$10^{40}\alpha^0_{el}$ / $C\,m^2\,V^{-1}$	4.14	3.66	5.63	13
$10^{40}\alpha^0_{est}$ / $C\,m^2\,V^{-1}$	4.15	4.06	5.66	
$10^{40}\alpha^0$ / $C\,m^2\,V^{-1}$	4.06	3.99	6.15	14

Finally, the experimental data presented here were found to be consistent with those obtained from a previous study by Kling, *et al*, and the analysis in combination with other data yielded reliable values of the polarizability components. The comparison of these values with those derived from other experimental and theoretical techniques is excellent, and an alternative indirect method of determining the static polarizabilities has been put forward.

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