*J. Phys. Chem. A* **2002,** *106,* 4257−4262

# Rayleigh Depolarization Ratios, Kerr Effects, Polarizabilities, and Hyperpolarizabilities of $CH_3Br$, $CH_2Br_2$, $CHBr_3$, and $CBr_4$. Comparison of Experimental and ab Initio Calculated Polarizabilities

**Ewan W. Blanch, Roland I. Keir, and Geoffrey L. D. Ritchie***

*Chemistry, University of New England, Armidale, NSW 2351, Australia*

*Received: January 7, 2002; In Final Form: February 22, 2002*

Improved equipment has been used to record the vapor-phase Rayleigh depolarization ratios and electrooptical Kerr effects of $CH_3Br$, $CH_2Br_2$, $CHBr_3$, and $CBr_4$ at elevated temperatures. The measurements yield experimental values of the anisotropic polarizabilities and the Kerr hyperpolarizabilities of these molecules. As well, Dougherty and Spackman's HUZ-SV(+sd+sp) basis set has been used to compute SCF and MP2-level polarizabilities, and these are compared with the experimental results.

## Introduction

Although the electric dipole polarizabilities and hyperpolarizabilities of the fluoro- and chloromethanes ($CH_{4-n}X_n$, X = F, Cl) can now be said to be reliably known,[1−11] the analogous bromo- and iodomethanes have not yet been systematically examined, despite their interest. The reasons are obvious: from an experimental viewpoint, the greatly diminished volatilities of the latter species militate against gas-phase observations; and, from a computational viewpoint, the sizes of the larger halogen atoms have posed significant problems as to the basis sets and the levels of theory that can be utilized. In the present study, improved equipment has been used to record the vapor-phase Rayleigh depolarization ratios (with and without inclusion of spurious vibrational Raman contributions[12]) and the temperature dependence of the vapor-phase electrooptical Kerr effects, at elevated temperatures, of the bromomethanes ($CH_{4-n}Br_n$) The measurements yield experimental values of the anisotropic polarizabilities ($\alpha_{xx}$, $\alpha_{yy}$, $\alpha_{zz}$) and the Kerr hyperpolarizabilities ($\beta^K$, $\gamma^K$) of these molecules. As well, CADPAC and the HUZ-SV (+sd+sp) basis set[13] have been used to compute SCF and MP2-level zero- and optical-frequency polarizabilities, and these are compared with the experimental results. Unfortunately, however, the iodomethanes ($CH_{4-n}I_n$) remain beyond the apparatus and procedures that are presently available.

## Theory

Note, first, that the principal axes of the molecular polarizability, shown in Figure 1, are defined such that *z*, the $C_3$ axis in $CH_3Br$ and $CHBr_3$ and the $C_2$ axis in $CH_2Br_2$, coincides with the direction (− to +) of the molecular dipole moment; in $CH_2Br_2$, *x* is in the HCH plane, and *y* is in the BrCBr plane.

The relationship between the Rayleigh depolarization ratio $\rho_0 = I_h^v/I_v^v$ and the optical-frequency molecular polarizability is[12]

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

in which $\kappa$ is the polarizability anisotropy parameter and

$$\alpha_{\alpha\alpha}/3 = \alpha = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 \quad (2)$$

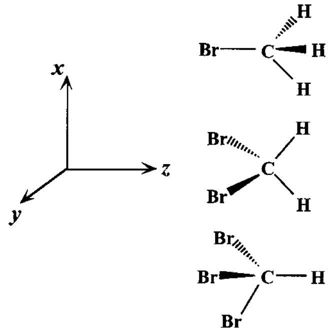

**Figure 1.** Definition of axes: *z* is the $C_3$ axis in $CH_3Br$ and $CHBr_3$ and the $C_2$ axis in $CH_2Br_2$; in $CH_2Br_2$, *x* is in the HCH plane and *y* is in the BrCBr plane.

is the mean polarizability. For the species of interest here, eq 1 can be formulated as

$$\kappa^2 = (\alpha_{zz} - \alpha_{xx})^2/9\alpha^2 \quad (3)$$

for $CH_3Br$ and $CHBr_3$ (in which $\alpha_{xx} = \alpha_{yy} \neq \alpha_{zz}$) and

$$\kappa^2 = [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2]/18\alpha^2 \quad (4)$$

for $CH_2Br_2$ (in which $\alpha_{xx} \neq \alpha_{yy} \neq \alpha_{zz}$) It is important to recall, too, that eq 1 requires that the rotational Raman spectrum of the scattered light be included in and the vibrational Raman spectrum be excluded from the measured intensities.[12]

The definition of the molar Kerr constant, ${}_{\rm m}K$, is[14,15]

$${}_{\rm m}K = 6nV_{\rm m}[(n^2+2)^2(\epsilon_{\rm r}+2)^2]^{-1}[(n_X - n_Y)F_X^{\ -2}]_{F_X=0} \quad (5)$$

where $n$ and $\epsilon_r$ are the refractive index and relative permittivity of the gas in the absence of the field; $n_X - n_Y$ is the birefringence for *XZ* and *YZ* polarized light that is induced by the uniform electric field, $F_X$; and $V_m$ is the molar volume. To take account of molecular interactions, ${}_{\rm m}K$ can be expressed in terms of $V_m$ as

$${}_{\rm m}K = A_{\rm K} + B_{\rm K}V_{\rm m}^{\ -1} + \ldots \quad (6)$$

in which $A_K$ and $B_K$ are the first and second Kerr virial

10.1021/jp020003t CCC: $22.00

coefficients; $A_K$ is the zero-density value of ${}_mK$ and $B_K$ measures the additional contribution to ${}_mK$ from interacting pairs of molecules. The first Kerr virial coefficient is, in SI units[15]

$$A_K = (N_A/81\epsilon_0)\{\gamma^K + (kT)^{-1}[(2/3)\mu\beta^K + (9/5)\alpha\alpha^0\kappa\kappa^0] + (3/10)(kT)^{-2}\mu^2(\alpha_{zz} - \alpha)\} \quad (7a)$$

$$= P + QT^{-1} + RT^{-2} \quad (7b)$$

where eq 7a relates $A_K$ to molecular properties and eq 7b emphasizes the quadratic dependence of $A_K$ on $T^{-1}$. As well, $\mu$ is the molecular dipole moment, $\alpha$ and $\alpha^0$ are the mean optical-frequency and static polarizabilities, $\alpha_{zz}$ is the component of $\alpha_{\alpha\beta}$ in the direction of $\mu$, $\kappa\kappa^0$ is the product of the optical-frequency and static polarizability anisotropy parameters, and $\beta^K$ and $\gamma^K$ are the first and second Kerr hyperpolarizabilities. The coefficients, $P$, $Q$, and $R$ are

$$P = (N_A/81\epsilon_0)\gamma^K \quad (8)$$

$$Q = (N_A/81\epsilon_0 k)[(2/3)\mu\beta^K + (9/5)\alpha\alpha^0\kappa\kappa^0] \quad (9)$$

$$R = (N_A/81\epsilon_0 k^2)(3/10)\mu^2(\alpha_{zz} - \alpha) \quad (10)$$

so that $P$ and $Q$ give $\gamma^K$ and $\beta^K$, respectively, and $R$ gives one of three necessary equations in $\alpha_{xx}$, $\alpha_{yy}$ and $\alpha_{zz}$; the other two are eq 2 together with either eq 3 or eq 4.

In relation to eq 7, it must be added, too, that unless the experimental data are of high precision and span a wide range of temperature, at least 200 K, it is difficult, if not impossible, to fit a quadratic equation such that all three coefficients are determined with the precision that is required for satisfactory analyses of eqs 8, 9, and 10. To date, this procedure has been performed only twice,[16] in both cases with excellent sets of data; and it is generally necessary, by one means or another, to reduce the quadratic equation to a linear equation, as has been done in the past.[1,4]

## Experimental Section

Samples were: $CH_3Br$ (Matheson, ≥ 99.4%) and $CHBr_3$ (Aldrich, ≥ 99%), used without further purification; $CH_2Br_2$ (Aldrich, 99%), washed several times (concentrated $H_2SO_4$, distilled water, 0.1 M NaOH, distilled water), dried over anhydrous $CaCl_2$ for 12 h, distilled from $P_2O_5$ and stored in the dark over molecular sieves; $CBr_4$ (BDH, > 98%), twice sublimed at 142 °C before use. Note that, under normal conditions, the sequence $CH_3Br$ (bp 4 °C), $CH_2Br_2$ (bp 97 °C), $CHBr_3$ (bp 150 °C) and $CBr_4$ (mp 90 °C) comprises a gas, two liquids and a solid; and the low volatilities of $CHBr_3$ and $CBr_4$, in particular, dictated that the measurements be performed at relatively high temperatures and low pressures.

Apparatus for measurements of the Rayleigh depolarization ratio, $\rho_0 = (I_h^v - I_{h,b}^v)/(I_v^v - I_{v,b}^v)$, of gases and vapors at 632.8 nm has been described.[17] Observations on $CH_3Br$ were made at 25 °C and ~100 kPa, on $CH_2Br_2$ at 25 °C and ~30 kPa, and on $CHBr_3$ at 86 °C and ~3.3 kPa. The results given below are the averages of repeated determinations, ~5 with inclusion and ~5 with exclusion by means of an interference filter of vibrational Raman contributions. Typical count rates (counts/s) without the filter in place for the depolarized and polarized signals, $I_h^v$ and $I_v^v$, and the backgrounds, $I_{h,b}^v$ and $I_{v,b}^v$, were as follows: $CH_3Br$, 700, 80 400, 8, 32; $CH_2Br_2$, 608, 39 100, 4, 25; and $CHBr_3$, 85, 8 700, 6, 29. Integration times were in the range 100−400 s. In the analysis of the data, the lower depolarization ratios (i.e., those that exclude vibrational Raman contributions) were used, because, as noted above, the theory of the effect was formulated on this basis.[12]

**TABLE 1: Temperature Dependence of the Vapor-State Kerr Effects of $CH_3Br$, $CH_2Br_2$, $CHBr_3$, and $CBr_4$ at 632.8 nm**

| $T$ (K) | no. of pressures | $p$ (kPa) | $B^a$ ($10^{-6}$ m$^3$ mol$^{-1}$) | $A_K$ ($10^{-27}$ m$^5$ V$^{-2}$ mol$^{-1}$) |
|---|---|---|---|---|
| | | | $CH_3Br$ | |
| 495.1 | 10 | 41−122 | −161 | 33.82 ± 0.05 |
| 470.6 | 10 | 39−121 | −181 | 37.21 ± 0.14 |
| 444.7 | 9 | 37−111 | −206 | 41.33 ± 0.09 |
| 414.6 | 11 | 37−114 | −244 | 47.54 ± 0.06 |
| 386.7 | 9 | 34−111 | −290 | 53.74 ± 0.06 |
| 365.6 | 11 | 38−111 | −336 | 59.13 ± 0.07 |
| 347.3 | 11 | 40−118 | −387 | 66.26 ± 0.34 |
| 332.2 | 10 | 40−114 | −438 | 72.78 ± 0.12 |
| 318.8 | 11 | 39−112 | −495 | 77.13 ± 0.07 |
| 306.3 | 10 | 34−107 | −548 | 83.26 ± 0.06 |
| 295.0 | 10 | 35−106 | −597 | 89.94 ± 0.09 |
| | | | $CH_2Br_2$ | |
| 500.2 | 9 | 39−84 | −253 | −5.42 ± 0.09 |
| 476.4 | 9 | 34−77 | −283 | −6.52 ± 0.09 |
| 465.8 | 10 | 28−59 | −298 | −6.75 ± 0.07 |
| 454.2 | 9 | 31−70 | −316 | −7.97 ± 0.07 |
| 439.2 | 10 | 33−71 | −341 | −9.04 ± 0.07 |
| 429.0 | 9 | 26−57 | −359 | −9.80 ± 0.05 |
| 405.5 | 9 | 25−55 | −406 | −11.47 ± 0.10 |
| 385.2 | 10 | 27−66 | −459 | −12.67 ± 0.05 |
| 378.9 | 11 | 26−63 | −475 | −13.72 ± 0.04 |
| 364.0 | 10 | 23−55 | −521 | −15.30 ± 0.21 |
| 360.1 | 10 | 27−59 | −533 | −15.51 ± 0.05 |
| | | | $CHBr_3$ | |
| 433.8 | 1 | 20.4 | | −8.05 ± 0.21 |
| 413.8 | 1 | 22.3 | | −9.30 ± 0.04 |
| 405.5 | 1 | 14.1 | | −9.96 ± 0.20 |
| 393.1 | 1 | 19.2 | | −11.70 ± 0.07 |
| 387.8 | 1 | 14.9 | | −11.99 ± 0.13 |
| 382.1 | 1 | 18.7 | | −12.,69 ± 0.08 |
| 374.2 | 1 | 17.3 | | −13.63 ± 0.06 |
| 367.4 | 1 | 15.2 | | −14.91 ± 0.16 |
| 354.6 | 1 | 9.5 | | −15.8 ± 0.8 |
| | | | $CBr_4$ | |
| 384.6 | 1 | 3.65 | | 2.2 ± 1.0 |

[a] Density second virial coefficients.

Equipment[16,18] for measurements of the temperature and pressure dependence of the electrooptical Kerr effect in gases and vapors was significantly improved by replacement of the original brass pressure vessel by a stainless steel version, reconstruction of the gas-handling system, introduction of a low-noise silicon photodiode in place of the photomultiplier tube, and use of a higher-powered He−Ne laser. In the cases of $CH_3Br$ and $CH_2Br_2$, it proved straightforward, although time-consuming, to measure the field-induced birefringences over a range of temperature and, at each temperature, over a range of pressure. However, in the case of $CHBr_3$ diminished volatility precluded examination of the pressure dependence; and in the case of $CBr_4$ greatly diminished volatility, thermal instability and the relatively small effect displayed by this nondipolar species limited the observations to a single temperature and pressure. The observed birefringences were used to establish values of ${}_mK_0 = (2/27)V_m(n_X - n_Y)F_X^{-2}$, and these were fitted to the relation[19]

$${}_mK_0 = A_K + \left[B_K + A_K\left(2A_\epsilon + \frac{1}{2}A_R\right)\right]V_m^{-1} \quad (11)$$

in which $A_\epsilon$ and $A_R$ are the low-density molar dielectric polarization and refraction, calculated from the static and optical-

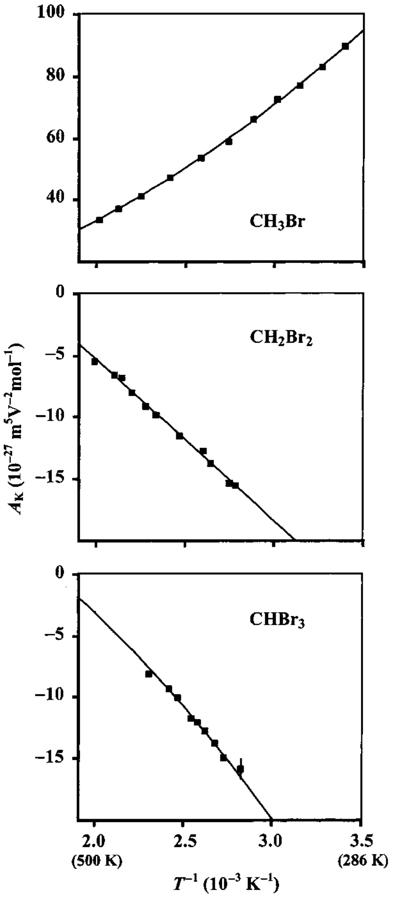

**Figure 2.** Temperature dependence of $A_K$ of $CH_3Br$, $CH_2Br_2$ and $CHBr_3$.

frequency molecular polarizabilities. For $CH_3Br$, reported density second virial coefficients,[20] augmented at higher temperatures by values calculated by means of a Stockmayer potential,[21] were used to allow for gas nonideality; for $CH_2Br_2$, in the absence of relevant experimental data, values calculated for $CH_2Cl_2$ by the method of Pitzer[22] were used; and for $CHBr_3$ and $CBr_4$ the effects of nonideality were assumed to be negligible under the conditions of the measurements The results are summarized in Table 1 and Figure 2, where the errors attributed to the values of $A_K$ are standard deviations obtained from the least-squares fitting of straight lines to the pressure-dependence data ($CH_3Br$, $CH_2Br_2$) or from direct averaging of the single-pressure data ($CHBr_3$, $CBr_4$); with calibration and other systematic errors the overall accuracy is estimated as ±3%. Even in the more favorable cases of $CH_3Br$ and $CH_2Br_2$, $B_K$ was poorly determined by the data, and estimates of this quantity are not reported here.

Vapor-phase Kerr constants have previously been given[23,24] for $CH_3Br$ at isolated temperatures in the vicinity of 300 K, and these are consistent with the present results for this species. In addition, dilute-solution Kerr constants are on record for $CH_3Br$,[25] $CH_2Br_2$,[26] and $CHBr_3$[27] as solutes in nondipolar solvents at 298 K; but local-field effects that occur in such solutions preclude a direct comparison of gas- and solution-phase data.[28]

## Results

**Depolarization Ratios and Polarizability Anisotropies.** Table 2 summarizes the depolarization ratios obtained in the present work with inclusion or exclusion of the vibrational Raman contributions (i.e., without or with the optical filter in place), the mean polarizabilities, and the derived polarizability anisotropies for the three anisotropic species. Previously reported depolarization ratios for $CH_3Br$ are also included and, clearly, the agreement is satisfactory. As expected, the vibrational Raman contribution is certainly significant for $CH_3Br$, only just significant for $CH_2Br_2$ and, in relation to the experimental errors, insignificant for $CHBr_3$. The individual components of the optical-frequency polarizabilities of $CH_3Br$ and $CHBr_3$ were obtained from eq 2 and 3, together with the usual bond-additivity assumption as to the sign of the anisotropy.

**TABLE 2: Depolarization Ratios and Polarizability Anisotropies of $CH_3Br$, $CH_2Br_2$, and $CHBr_3$ at 632.8 nm**

| | value | | |
|---|---|---|---|
| property | $CH_3Br$ | $CH_2Br_2$ | $CHBr_3$ |
| $\rho_0(10^{-2})$(vib. Raman incl.) | $0.863 \pm 0.006$<br>$0.85 \pm 0.01$[a]<br>$0.865 \pm 0.010$[b] | $1.53 \pm 0.01$ | $0.90 \pm 0.04$ |
| $\rho_0(10^{-2})$(vib. Raman excl.) | $0.840 \pm 0.003$ | $1.49 \pm 0.02$ | $0.91 \pm 0.03$ |
| $\kappa^2(10^{-2})$[c] | $1.416 \pm 0.005$ | $2.53 \pm 0.03$ | $1.54 \pm 0.05$ |
| $\alpha(10^{-40}\ \mathrm{C\ m^2\ V^{-1}})$ | $6.22 \pm 0.03$[b] | $9.62 \pm 0.05$[d] | $13.11 \pm 0.07$[d] |
| $\lvert\Delta\alpha\rvert$[e] | $2.22 \pm 0.01$ | $4.59 \pm 0.04$ | $4.87 \pm 0.08$ |
| $\alpha_{zz}$ | $7.70 \pm 0.03$ | | $9.86 \pm 0.09$ |
| $\alpha_{xx}$ | $5.48 \pm 0.03$ | | $14.73 \pm 0.07$ |

[a] Ref 24; $\lambda = 488$ nm. [b] Ref 5. [c] Eq 1. [d] Calculated as $\alpha = (3\epsilon_0/N_A)_mR$ from interpolated liquid-state molar refractions ($_mR/10^{-6}$ m$^3$ mol$^{-1}$) for $\lambda = 632.8$ nm ($CH_2Br_2$, 21.80; $CHBr_3$, 29.72), uncertainties estimated as ± 0.5%; Vogel, A. I. *J. Chem. Soc.* **1948**, 1833−1855. [e] Polarizability anisotropy $|\Delta\alpha| = |9\alpha\,\kappa| = |\alpha_{zz} - \alpha_{xx}|$ ($CH_3Br$, $CHBr_3$) or $|[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2]^{1/2}/\sqrt{2}|$ ($CH_2Br_2$).

**Temperature Dependence of Kerr Effects.** For the nondipolar and isotropically polarizable species $CBr_4$, eq 7 reduces to $A_K = (N_A/81\epsilon_0)\gamma^K$ and, from the measured Kerr constant ($\sim A_K$) in Table 1, $\gamma^K = (2.6 \pm 1.2) \times 10^{-60}$ C m$^4$ V$^{-3}$. Note that the large uncertainty in this result is a consequence of the smallness of the Kerr effect that was manifested under the conditions of temperature and pressure that were achievable for this involatile compound.

In the earlier studies[1,4] of the dipolar and anisotropically polarizable species $CH_3X$, $CH_2X_2$, and $CHX_3$ (X = F, Cl), the number of unknowns in eq 7 was reduced by one, and a quadratic equation thereby reduced to a much simpler linear equation, by means of a bond-additivity approximation for $\gamma^K$, a small but not negligible contributor to $A_K$. Unfortunately, the same approach is of doubtful validity for $CH_3Br$, $CH_2Br_2$, and $CHBr_3$, for obvious reasons. First, the values of $\gamma^K$ for $CH_4$ and $CBr_4$ differ by more than an order of magnitude and the larger of the two is of low precision; and, second, the $\gamma^K$ term makes a proportionately larger contribution to $A_K$, especially for $CH_2Br_2$ and $CHBr_3$ (∼−5% at 300 K). A reliable alternative is, however, available for $CH_3Br$ and $CHBr_3$, although not for $CH_2Br_2$.

In the cases of $CH_3Br$ and $CHBr_3$, which possess a 3-fold axis of symmetry

$$\alpha_{zz} - \alpha = (2/3)(\alpha_{zz} - \alpha_{xx}) - (2/3)\Delta\alpha \qquad (12)$$

and, because $\Delta a$ is known (Table 2), eq 7 can be rewritten as

$$A_K - (N_A/405\epsilon_0 k^2)\mu^2(\Delta\alpha)T^{-2}$$

$$= (N_A/81\epsilon_0)\{\gamma^K + (kT)^{-1}[(2/3)\mu\beta^K + (9/5)\alpha\alpha^0\kappa\kappa^0]\} \qquad (13a)$$

$$= P + QT^{-1} \qquad (13b)$$

a linear equation in $T^{-1}$ such that the intercept, $P$, and the slope,

**TABLE 3: Analysis of the Temperature Dependence of $A_K$ of $CH_3Br$, $CH_2Br_2$, and $CHBr_3$ at 632.8 nm**

| | value | | |
|---|---|---|---|
| property | $CH_3Br$ | $CH_2Br_2$ | $CHBr_3$ |
| $P(10^{-27}\ \mathrm{m^5\ V^{-2}\ mol^{-1}})^{a}$ | $1.2 \pm 0.7^{d}$ | | $1.5 \pm 1.1^{d}$ |
| $Q(10^{-24}\ \mathrm{m^5\ V^{-2}\ mol^{-1}\ K})^{b}$ | $1.60 \pm 0.25^{d}$ | $3.47 \pm 0.36^{e}$ | $6.88 \pm 0.45^{d}$ |
| $R(10^{-21}\ \mathrm{m^5\ V^{-2}\ mol^{-1}\ K^2})^{c}$ | | $-3.45 \pm 0.15^{e}$ | |
| $\gamma^{K}(10^{-60}\ \mathrm{C\ m^4\ V^{-3}})$ | $1.5 \pm 0.8$ | $1.5 \pm 0.3^{f}$ | $1.8 \pm 1.4$ |
| $\alpha(10^{-40}\ \mathrm{C\ m^2\ V^{-1}})$ | $6.22 \pm 0.03$ | $9.62 \pm 0.05$ | $13.11 \pm 0.07$ |
| $\alpha^0(10^{-40}\ \mathrm{C\ m^2\ V^{-1}})^{g}$ | $6.17 \pm 0.06$ | $9.72 \pm 0.10$ | $13.54 \pm 0.14$ |
| $\kappa$ | $0.119 \pm 0.000$ | $0.159 \pm 0.002$ | $0.124 \pm 0.002$ |
| $\kappa^{0g}$ | $0.123 \pm 0.000$ | $0.176 \pm 0.004$ | $0.140 \pm 0.004$ |
| $\mu(10^{-30}\ \mathrm{C\ m})$ | $6.0768 \pm 0.0012^{h}$ | $4.75 \pm 0.07^{i}$ | $3.31 \pm 0.08^{i}$ |
| $\beta^{K}(10^{-50}\ \mathrm{C\ m^3\ V^{-2}})$ | $0.4 \pm 0.1$ | $0.3 \pm 0.2$ | $2.6 \pm 0.4$ |
| $\alpha_{zz}(10^{-40}\ \mathrm{C\ m^{2\ V^{-1}}})^{j}$ | $7.70 \pm 0.03$ | $8.46 \pm 0.07^{k}$ | $9.86 \pm 0.09$ |
| $\alpha_{xx}$ | $5.48 \pm 0.03$ | $7.74 \pm 0.14$ | $14.73 \pm 0.07$ |
| $\alpha_{yy}$ | $5.48 \pm 0.03$ | $12.65 \pm 0.14$ | $14.73 \pm 0.07$ |

[a] Eq 8. [b] Eq 9. [c] Eq 10. [d] Eq 13. [e] Eq 14. [f] Assumed value. A weighted least-squares fit to the measured values of $\gamma^K$ ($10^{-60}$ C m$^4$ V$^{-3}$) for $CH_4$ ($0.180 \pm 0.009$, ref 1), $CH_3Br$, $CHBr_3$ and $CBr_4$ gave the relationship with the number of Br atoms, $n$, as $\gamma^K$ ($10^{-60}$ C m$^4$ V$^{-3}$) $= (0.18 \pm 0.01) + (0.65 \pm 0.14)\,n$, from which the value for $CH_2Br_2$ was interpolated. [g] Calculated from the computed dispersion in the electronic polarizabilities and estimates of the contribution of the vibrational polarizabilities (ref 29). [h] Ref 30. [i] Ref 31. [j] Locations of axes: $z$, the $C_3$ axis in $CH_3Br$ and $CHBr_3$ and the $C_2$ axis in $CH_2Br_2$, is the direction of the dipole moment; in $CH_2Br_2$, $x$ is in the HCH plane and $y$ is in the BrCBr plane (Figure 1). [k] Values of $\alpha_{zz}$, $\alpha_{xx}$, $\alpha_{yy}$ derived by simultaneous solution of three independent equations in the three unknowns (see text).

$Q$, yield $\gamma^K$ and $\beta^K$, respectively. In the case of $CH_2Br_2$, eq 12 is not valid and, as previously,[1] eq 7 was rewritten as

$$[A_K - (N_A/81\epsilon_0)\gamma^K]T$$

$$= (N_A/81\epsilon_0 k)\{[(2/3)\mu\beta^K + (9/5)\alpha\alpha^0\kappa\kappa^0] + (3/10k)\mu^2(\alpha_{zz} - \alpha)T^{-1}\} \quad (14a)$$

$$= Q + RT^{-1} \quad (14b)$$

a linear equation in $T^{-1}$ such that the intercept, $Q$, and the slope, $R$, yield $\beta^K$ and $\alpha_{zz} - \alpha$, respectively. However, the assumed value of $\gamma^K$ for $CH_2Br_2$ on the left-hand side was interpolated from a weighted fit of the measured values for $CH_4$,[1] $CH_3Br$, $CHBr_3$, and $CBr_4$, and so is more reliable than if a bond-additivity estimate based on only $CH_4$ and $CBr_4$ were used.

Table 3 contains, for $CH_3Br$ and $CHBr_3$, the coefficients $P$ and $Q$ from eq 13 and, for $CH_2Br_2$, the coefficients $Q$ and $R$ from eq 14, together with analyses of these in terms of molecular properties. Other data shown are the mean optical-frequency and static polarizabilities, $\alpha$ and $\alpha^0$; the optical-frequency and static polarizability anisotropy parameters, $\kappa$ and $\kappa^0$, the latter derived from the computed dispersion in the electronic polarizabilities (see below) and estimates of the contribution of the vibrational polarizabilities;[29] and the molecular dipole moments.[30,31] The new results are the values of $\gamma^K$ for $CH_3Br$ and $CHBr_3$ (and $CBr_4$), the values of $\beta^K$ for $CH_3Br$, $CH_2Br_2$, and $CHBr_3$, and the values of $\alpha_{xx}$, $\alpha_{yy}$, and $\alpha_{zz}$ for $CH_2Br_2$. Note that simultaneous solution of eqs 2, 4, and 10, of which eq 4 is quadratic, yields two possible sets of polarizabilities that satisfy the equations. The choice between the two involves the bond-additivity assumption that the polarizability is greater along than across the C−Br bonds in $CH_2Br_2$ so that $\alpha_{yy} \gg \alpha_{xx}$, as indicated. Table 4 summarizes the absolute and percentage contributions of the four terms in eq 7 to the value of $A_K$ at 300 K. For each of these species the observed effect is once again dominated by the $\mu^2(\alpha_{zz} - \alpha)$ term, with smaller contributions from the $\mu\beta^K$, $\alpha\alpha^0\kappa\kappa^0$ and $\gamma^K$ terms.

**TABLE 4: Contributions to $A_K$ of $CH_3Br$, $CH_2Br_2$, and $CHBr_3$ at 300 K**

| | value ($10^{-27}$ m$^5$ V$^{-2}$ mol$^{-1}$) | | |
|---|---|---|---|
| term | $CH_3Br$ | $CH_2Br_2$ | $CHBr_3$ |
| $(N_A/81\epsilon_0)\gamma^K$ | 1.2<br>(+1.4%) | 1.2<br>(−4.9%) | 1.5<br>(−5.5%) |
| $(2N_A/243\epsilon_0 kT)\mu\beta^K$ | 3.3<br>(+3.8%) | 2.0<br>(−7.9%) | 11.7<br>(−41.9%) |
| $(N_A/45\epsilon_0 kT)\alpha\alpha^0\kappa\kappa^0$ | 2.1<br>(+2.4%) | 9.6<br>(−37.5%) | 11.2<br>(−40.3%) |
| $(N_A/270\epsilon_0 k^2T^2)\mu^2(\alpha_{zz} - \alpha)$ | 80.2<br>(+92.4%) | −38.3<br>(+150.3%) | −52.3<br>(+187.7%) |
| $A_K$ | 86.8 | −25.5 | −27.9 |

**TABLE 5: Calculated and Experimental Structures of $CH_4$, $CH_3Br$, $CH_2Br_2$, $CHBr_3$, and $CBr_4$[a]**

| | value | |
|---|---|---|
| property | calcd | exp[b] |
| | $CH_4$ | |
| C−H | 0.1089 | 0.1087 ($r_e$) |
| | $CH_3Br$ | |
| C−H | 0.1087 | 0.1086 ($r_e$) |
| C−Br | 0.1950 | 0.1933 ($r_e$) |
| HCH | 111.0 | 111.2 |
| | $CH_2Br_2$ | |
| C−H | 0.1085 | 0.1079 ($r_s$) |
| C−Br | 0.1941 | 0.1927 ($r_s$) |
| BrCBr | 113.3 | 112.7 |
| | $CHBr_3$ | |
| C−H | 0.1086 | 0.1068 ($r_0$) |
| C−Br | 0.1940 | 0.1930 ($r_0$) |
| BrCBr | 111.6 | 110.8 |
| | $CBr_4$ | |
| C−Br | 0.1951 | 0.1942 ($r_g$) |

[a] Bond lengths in nm, angles in degrees. [b] Reference 34.

**Calculations of Polarizabilities.** Ab initio calculations of the polarizabilities of $CH_4$, $CH_3Br$, $CH_2Br_2$, $CHBr_3$, and $CBr_4$ were undertaken to complement the experimental study reported above and as a further test of Dougherty and Spackman's HUZ-SV (+sd+sp) basis set,[13] which was specially developed for the electric properties of such molecules. To date, the bromomethanes have received little attention ($CH_3Br$;[13,32] $CHBr_3$[33]). Optimized geometries for the five molecules of interest were obtained with the HUZ-SV** basis set and, as can be seen from Table 5, the agreement with the experimental geometries[34,35] is satisfactory. Computations of the SCF and MP2-level zero- and optical-frequency polarizabilities with the HUZ-SV(+sd+sp) basis set followed the procedures of earlier investigations.[13,36] Because the present concern is the comparison, shown in Table 6, of results from experiment and theory, only the optical-

**TABLE 6: Calculated and Experimental Polarizabilities of $CH_4$, $CH_3Br$, $CH_2Br_2$, $CHBr_3$, and $CBr_4$ at 632.8 nm**

| | value ($10^{-40}$ C m$^2$ V$^{-1}$) | | |
|---|---|---|---|
| property | SCF | MP2 | exp |
| | $CH_4$ | | |
| $\alpha$ | 2.647 | 2.758 (−4.9%)[a] | 2.901 ± 0.000[b] |
| | $CH_3Br$ | | |
| $\alpha$ | 5.835 | 6.138 (−1.3%) | 6.22 ± 0.03 |
| $\alpha_{zz}$ | 7.506 | 7.687 (−0.2%) | 7.70 ± 0.03 |
| $\alpha_{xx}$ | 5.000 | 5.363 (−2.1%) | 5.48 ± 0.03 |
| $\Delta\alpha$ | 2.507 | 2.324 (+4.7%) | 2.22 ± 0.01 |
| | $CH_2Br_2$ | | |
| $\alpha$ | 9.154 | 9.685 (+0.7%) | 9.62 ± 0.05 |
| $\alpha_{zz}$ | 7.993 | 8.507 (+0.6%) | 8.46 ± 0.07 |
| $\alpha_{xx}$ | 7.088 | 7.687 (−0.7%) | 7.74 ± 0.14 |
| $\alpha_{yy}$ | 12.380 | 12.860 (+1.7%) | 12.65 ± 0.14 |
| $\Delta\alpha$ | 4.903 | 4.816 (+4.9%) | 4.59 ± 0.04 |
| | $CHBr_3$ | | |
| $\alpha$ | 12.438 | 13.189 (+0.6%) | 13.11 ± 0.07 |
| $\alpha_{zz}$ | 9.172 | 9.941 (+0.8%) | 9.86 ± 0.09 |
| $\alpha_{xx}$ | 14.072 | 14.814 (+0.6%) | 14.73 ± 0.07 |
| $\Delta\alpha$ | −4.900 | −4.873 (−0.0%) | −4.87 ± 0.08 |
| | $CBr_4$ | | |
| $\alpha$ | 15.718 | 16.681 (−0.1%) | 16.70 ± 0.17 [c] |

[a] Percentage deviation of MP2-level calculated value from experimental value. [b] Hohm, U. *Mol. Phys.* **1993**, *78*, 929−941. [c] Extrapolated from the experimental values for $CH_4$, $CH_3Br$, $CH_2Br_2$, and $CHBr_3$ given above.

frequency (632.8 nm) polarizabilities are reported here. Note, too, that the computed polarizabilities specifically exclude vibrational effects, i.e., zero-point averaging and pure vibrational contributions.

## Discussion

In relation to the optical-frequency molecular polarizabilities, the results summarized in Tables 3 and 6 comprise the first systematic investigation of the bromomethanes, and this supplements earlier investigations of the fluoro- and chloromethanes, noted above. The experimental values have been obtained with acceptable precision and, clearly, the comparison with the theoretical values obtained at the MP2 level with the purpose-designed HUZ-SV(+sd+sp) basis set is satisfactory. In each of the series $CH_3X$, $CH_2X_2$, and $CHX_3$ (X = F, Cl, Br), replacement of F by Cl and, in turn, Br further enhances the polarizability along the axis of the C−X bond or bonds, and so increases the magnitude of the polarizability anisotropy.

The molecular hyperpolarizabilities were, once again, less well determined, but some useful conclusions can nevertheless be drawn. For example, the present value of $\gamma^K$ for $CBr_4$ confirms that in the series $CX_4$ (X = H, F, Cl, Br) there is a roughly linear relationship between $\gamma^K$ (expressed here as $\gamma^K/10^{-60}$ C m$^4$ V$^{-3}$) and the molecular size as measured by the mean polarizability *a* (expressed here as $\alpha/10^{-40}$ C m$^2$ V$^{-1}$): H, 0.180 ± 0.009, 2.901;[1] F, 0.093 ± 0.005, 3.172;[1] Cl, 1.23 ± 0.04, 11.69;[4] Br, 2.6 ± 1.2, 16.70. As well, the measured values of $\gamma^K$ for $CH_4$, $CH_3Br$, $CHBr_3$ and $CBr_4$ conform to a simple bond-additivity model and show a more or less linear relationship with the number of Br atoms, a fact that was used to advantage to estimate $\gamma^K$ for $CH_2Br_2$. The values of $\beta^K$ for $CH_3Br$, $CH_2Br_2$ and $CHBr_3$ are thought to be reliable: but the result for $CHBr_3$ is certainly larger than anticipated. Unfortunately, it is not yet possible to discern trends in $\beta^K$ associated with progressive introduction of a particular halogen, or with replacement of one halogen by another in a particular series.

Finally, it is appropriate to reiterate that, for reasons that have been elaborated here and elsewhere, the temperature dependence of the electrooptical Kerr effect is enormously useful in relation to the anisotropy in the molecular polarizability, but much less useful in relation to the molecular hyperpolarizabilities. The main reason that this is so, at least for anisotropically polarizable species, is that the hyperpolarizabilities are usually deeply embedded as minor contributors to the observed effect; and their separation and recovery from the major contributors with acceptable precision pose significant difficulties, as has been further demonstrated by this investigation.

**Acknowledgment.** An Australian Postgraduate Award (to R.I.K.) and the assistance of Professor M. A. Spackman with the ab initio calculations are gratefully acknowledged.

## References and Notes

(1) Buckingham, A. D.; Orr, B. J. *Trans. Faraday Soc.* **1969**, *65*, 673−681.

(2) Ward, J. F.; Bigio, I. J. *Phys. Rev. A* **1975**, *11*, 60−66.

(3) Miller, C. K.; Ward, J. F. *Phys. Rev. A* **1977**, *16*, 1179−1185.

(4) Bogaard, M. P.; Orr, B. J.; Buckingham, A. D.; Ritchie, G. L. D. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1573−1578.

(5) Bogaard, M. P.; Buckingham, A. D.; Pierens, R. K.; White, A. H. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 3008−3015.

(6) Orr, B. J. Hyperpolarizabilities of Halogenated Methane Molecules: A Critical Survey. In *Nonlinear Behaviour of Molecules, Atoms and Ions in Electric, Magnetic or Electromagnetic Fields*; Néel, L., Ed.; Elsevier: Amsterdam, 1979; pp 227−235.

(7) Miller, C. K.; Orr, B. J.; Ward, J. F. *J. Chem. Phys.* **1981**, *74*, 4858−4871.

(8) Ward, J. F.; Elliott, D. S. *J. Chem. Phys.* **1984**, *80*, 1003−1005.

(9) Spackman, M. A. *J. Phys. Chem.* **1989**, *93*, 7594−7603.

(10) For a review of measurements and calculations of $\beta$ and $\gamma$ for gas-phase species see: Shelton, D. P.; Rice, J. E. *Chem. Rev.* **1994**, *94*, 3−29.

(11) Russell, A. J.; Spackman, M. A. *Mol. Phys.* **2000**, *98*, 633−642.

(12) Bridge, N. J.; Buckingham, A. D. *Proc. R. Soc. London, Ser. A* **1966**, *295*, 334−349.

(13) Dougherty, J.; Spackman, M. A. *Mol. Phys.* **1994**, *82*, 193−209.

(14) Otterbein, G. *Phys. Z.* **1934**, *35*, 249−265.

(15) (a) Buckingham, A. D.; Pople, J. A. *Proc. Phys. Soc. A* **1955**, *68*, 905−909. (b) Buckingham, A. D. *Proc. Phys. Soc. A* **1955**, *68*, 910−919.

(16) (a) Gentle, I. R.; Laver, D. R.; Ritchie, G. L. D. *J. Phys. Chem.* **1990**, *94*, 3434−3437. (b) Couling, V. W.; Halliburton, B. W.; Keir, R. I.; Ritchie, G. L. D. *J. Phys. Chem.* **2001**, *105*, 4365−4370.

(17) Keir, R. I.; Ritchie, G. L. D. *Chem. Phys. Lett.* **1998**, *290*, 409−414.

(18) (a) Gentle, I. R.; Laver, D. R.; Ritchie, G. L. D. *J. Phys. Chem.* **1989**, *93*, 3035−3038. (b) Gentle, I. R.; Ritchie, G. L. D. *J. Phys. Chem.* **1989**, *93*, 7740−7744.

(19) Buckingham, A. D.; Orr, B. J. *Proc. R. Soc. London Ser. A* **1968**, *305*, 259−269.

(20) Dymond, J. H.; Smith, E. B. *The Virial Coefficients of Pure Gases and Mixtures*; Clarendon Press: Oxford, U.K., 1980.

(21) Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. *Molecular Theory of Gases and Liquids*; Wiley: New York, 1964.

(22) Pitzer, K. S.; Lippmann, D. Z.; Curl, R. F.; Huggins, C. M.; Petersen, D. E. *J. Am. Chem. Soc.* **1955**, *77*, 3433−3440.

(23) (a) Stuart, H. A. *Z. Phys.* **1929**, *55*, 13−34. (b) Stuart, H. A. *Z. Phys.* **1930**, *63*, 533−557.

(24) Burnham, A. K.; Buxton, L. W.; Flygare, W. H. *J. Chem. Phys.* **1977**, *67*, 4990−4995.

(25) Le Fèvre, C. G.; Le Fèvre, R. J. W. *J. Chem. Soc.* **1954**, 1577−1588.

(26) Izsak, D.; Le Fèvre, R. J. W. *J. Chem. Soc. (B)* **1966**, 102−106.

(27) Le Fèvre, R. J. W.; Ritchie, G. L. D. *J. Chem. Soc.* **1963**, 4933−4938.

(28) Buckingham, A. D.; Stiles, P. J.; Ritchie, G. L. D. *Trans. Faraday Soc.* **1971**, *67*, 577−582.

(29) Bishop, D. M.; Cheung, L. M. *J. Phys. Chem. Ref. Data* **1982**, *11*, 119−133.

(30) Carocci, S.; Minguzzi, P.; Tonelli, M.; Di Lieto, A. *J. Mol. Spectrosc.* **1993**, *160*, 359−370.

(31) Buckingham, A. D.; Le Fèvre, R. J. W. *J. Chem. Soc.* **1953**, 3432−3435.

(32) Packer, M. J.; Dalskov, E. K.; Sauer, S. P. A.; Oddershede, J. *Theor. Chim. Acta* **1994,** *89*, 323−333.

(33) (a) Karna, S. P.; Dupuis, M.; Perrin, E.; Prasad, P. N. *J. Chem. Phys*. **1990**, *92*, 7418−7425. (b) Karna, S. P.; Dupuis, M. *Chem. Phys. Lett.* **1990**, *171*, 201−208. (c) Karna, S. P.; Perrin, E.; Prasad, P. N.; Dupuis, M. *J. Phys. Chem.* **1991**, *95*, 4329−4332.

(34) *Landolt-Börnstein Numerical Data and Functional Relationships in Science and Technology*; New Series, Group II, Vol. 23, Structure Data of Free Polyatomic Molecules; Springer: Berlin, 1995.

(35) Venkatraman, R.; Kwiatkowski, J. S.; Bakalarski, G.; Leszczynski, J. *Mol. Phys*. **2000**, *98*, 371−386.

(36) Coonan, M. H.; Craven, I. E.; Hesling, M. R.; Ritchie, G. L. D.; Spackman, M. A. *J. Phys. Chem.* **1992**, *96*, 7301−7307.