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Temperature Dependence of the Electrooptical Kerr Effect: Anisotropic Electric Dipole Polarizabilities of NH_3, CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$

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The study that is reported here is concerned with the development of an experimental route to the four independent components of the electric dipole polarizability of species of C_s symmetry and, in particular, with the specification of the anisotropic polarizabilities of NH_3, CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$, for which a consistent set of data has not been available. It is shown that the four equations required to evaluate the four components of the optical-frequency ($\lambda = 632.8$ nm) polarizabilities of CH_3NH_2 and $(CH_3)_2NH$ can be drawn from measurements of (1) the temperature dependence of the electrooptical Kerr effect, (2) the Rayleigh depolarization ratio, and (3) the refractive index of the gas together with (4) a simple bond-additivity model of the polarizability. The model uses the polarizabilities of the C_{3v} species NH_3 and $(CH_3)_3N$ to estimate the off-diagonal polarizabilities of the C_s species CH_3NH_2 and $(CH_3)_2NH$. To this end, improved equipment has been used to record the vapor-phase Kerr effects of NH_3, CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$ over ranges of temperature and pressure. An analysis of the data yields precise values of the anisotropic polarizabilities and, as a bonus, less precise values of the Kerr hyperpolarizabilities of all four molecules and provides a clear demonstration of the utility of the method.

Introduction

Although the anisotropic electric dipole polarizabilities of a useful number and variety of asymmetric tops (i.e., $\alpha_{xx} \neq \alpha_{yy} \neq \alpha_{zz}$) have now been evaluated by experiment, reliable data for important molecules of C_s symmetry (e.g., CH_3CHO,[1] CH_3OH, CH_3NH_2, CH_3CH_2F) have generally been unavailable. The reason that this is so is primarily that, in relation to reference axes that are not coincident with the principal axes of the tensor, the polarizability of a species of this symmetry has four, not three, independent components ($\alpha_{xx} \neq \alpha_{yy} \neq \alpha_{zz} \neq \alpha_{xy}$)[2] and one of these ($\alpha_{xy}$) is normally much smaller and, at least experimentally, much less accessible than the others. Moreover, the locations of the two in-plane principal axes are not obvious from the molecular structure, and they will not necessarily coincide with the principal axes of the moment of inertia or any other molecular property that transforms as a second-order tensor. The study that is reported here focuses on the experimental determination of the free-molecule anisotropic polarizabilities of NH_3, CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$, of which NH_3 and $(CH_3)_3N$ have C_{3v} symmetry and CH_3NH_2 and $(CH_3)_2NH$ have C_s symmetry; only NH_3 has previously been examined. It is shown that the four equations required to evaluate the four components of the polarizabilities of CH_3NH_2 and $(CH_3)_2NH$ can be drawn from measurements of (1) the temperature dependence of the Kerr constant, (2) the Rayleigh depolarization ratio, and (3) the refractive index together with (4) a simple bond-additivity model. The model uses the polarizabilities of the symmetrical species NH_3 and $(CH_3)_3N$, newly determined here, to estimate the off-diagonal polarizabilities of the less symmetrical species CH_3NH_2 and $(CH_3)_2NH$. The complete analysis of the data yields precise values of the anisotropic polarizabilities and, as a bonus, less precise values of the Kerr hyperpolarizabilities of all four molecules and provides a clear demonstration of the utility of the method.

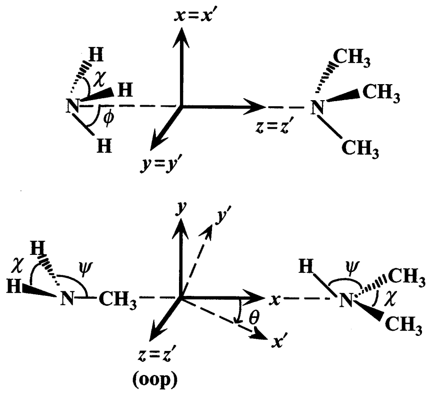

Figure 1. Locations of axes (oop = out-of-plane): *x*, *y*, *z* = reference axes; *x*′, *y*′, *z*′ = principal axes. For NH_3 and $(CH_3)_3N$ (C_{3v}), *z* is the C_3 axis; for CH_3NH_2 (C_s), *x* coincides with the N−CH_3 bond, and for $(CH_3)_2NH$ (C_s), *x* bisects ∠ CNC.

Theory

It is necessary, first, to choose convenient reference axes (*x*, *y*, *z*) and, as well, to identify the geometrical relationship of these to the principal axes (*x*′, *y*′, *z*′) of the polarizability tensors of NH_3, CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$, as shown in Figure 1. In the cases of NH_3 and $(CH_3)_3N$ (C_{3v} symmetry), the principal axes are defined by the symmetry, but in the cases of CH_3NH_2 and $(CH_3)_2NH$ (C_s symmetry), only the $z = z'$ (out-of-plane) principal axis, which is perpendicular to the plane of symmetry, is immediately obvious; the locations of the *x*′ and *y*′ principal axes in this plane are not obvious. It is useful to recognize, too, that for CH_3NH_2 and $(CH_3)_2NH$ the reference axes in Figure 1 are judicious choices in that only the H atoms

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bonded to N contribute to the single off-diagonal element, α_{xy}, of the polarizability. The angles, θ, through which the reference axes x and y must be rotated to locate the principal axes x' and y' can therefore be expected to be small. Note, also, that the directions of action of the dipole moments, μ, of these molecules are such that, for NH_3 and $(CH_3)_3N$, $\mu_x = \mu_y = 0$, $\mu_z = \mu$ and, for CH_3NH_2 and $(CH_3)_2NH$, $\mu_x \neq \mu_y \neq 0$, $\mu_z = 0$.

The polarizabilities of NH_3 and $(CH_3)_3N$ have only two nonzero components, α_{xx} ($= \alpha_{yy}$) and α_{zz}, so that the tensors are completely specified by any two independent equations that connect these to physical observables. However, in the reference axis systems shown in Figure 1, the polarizabilities of CH_3NH_2 and $(CH_3)_2NH$ have four nonzero components, α_{xx}, α_{yy}, α_{zz}, and α_{xy}, and four such equations are required. In principle, these could be drawn from measurements of (1) the temperature dependence of the Kerr constant, A_K, (2) the Rayleigh depolarization ratio, ρ_0, and (3) the refractive index or mean polarizability,α, together with (4) a simple bond-additivity model, described in the next section, that uses the polarizabilities of the symmetrical species NH_3 and $(CH_3)_3N$ to estimate the off-diagonal polarizabilities of the less symmetrical species CH_3NH_2 and $(CH_3)_2NH$.

The classical statistical-mechanical expression[4] for the zero-density Kerr constant, A_K, does not require or imply any particular choice of molecule-fixed axes. For the axis systems defined in Figure 1, this quantity can be formulated for NH_3 and $(CH_3)_3N$ as

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

and for CH_3NH_2 and $(CH_3)_2NH$ as

$$A_K = \left(\frac{N_A}{81\epsilon_0}\right)\left\{\gamma^K + (kT^{-1})\left[\left(\frac{2}{3}\right)\mu\beta^K + \left(\frac{9}{5}\right)\alpha\alpha^0\kappa\kappa^0\right] + \left(\frac{3}{10}\right)(kT)^{-2}[\mu_x^2(\alpha_{xx} - \alpha) + \mu_y^2(\alpha_{yy} - \alpha) + 2\mu_x\mu_y\alpha_{xy}]\right\} \tag{1b}$$

in which α and α^0 are the mean optical-frequency and static polarizabilities, $\kappa\kappa^0$ ($\approx \kappa^2$) is the product of the optical-frequency and static polarizability anisotropy parameters,[5] β^K and γ^K are the first and second Kerr hyperpolarizabilities,[6] and SI units are implied.[7] Equations 1a and 1b have the form

$$A_K = P + QT^{-1} + RT^{-2} \tag{2}$$

where

$$P = \left(\frac{N_A}{81\epsilon_0}\right)\gamma^K \tag{3}$$

$$Q = \left(\frac{N_A}{81\epsilon_0 k}\right)\left[\left(\frac{2}{3}\right)\mu\beta^K + \left(\frac{9}{5}\right)\alpha\alpha^0\kappa\kappa^0\right] \tag{4}$$

and for NH_3 and $(CH_3)_3N$

$$R = \left(\frac{N_A}{81\epsilon_0 k^2}\right)\left(\frac{3}{10}\right)\mu_z^2(\alpha_{zz} - \alpha) \tag{5a}$$

or for CH_3NH_2 and $(CH_3)_2NH$

$$R = \left(\frac{N_A}{81\epsilon_0 k^2}\right)\left(\frac{3}{10}\right)[\mu_x^2(\alpha_{xx} - \alpha) + \mu_y^2(\alpha_{yy} - \alpha) + 2\mu_x\mu_y\alpha_{xy}] \tag{5b}$$

so that, if all of the other quantities are known, P and Q give γ^K and β^K, respectively, and R gives the desired equation in the components of the polarizability. The relationships between κ^2 and the polarizability are, for NH_3 and $(CH_3)_3N$,

$$\kappa^2 = \frac{[(\alpha_{zz} - \alpha_{xx})^2]}{9\alpha^2} \tag{6a}$$

or, for CH_3NH_2 and $(CH_3)_2NH$,

$$\kappa^2 = \frac{[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xy}^2]}{18\alpha^2} \tag{6b}$$

where

$$\alpha = \frac{(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})}{3} \tag{7}$$

is the mean polarizability.[3] The procedure employed here to evaluate the two components of the polarizabilities of NH_3 and $(CH_3)_3N$ therefore involves the simultaneous solution of eqs 5a and 7; that for the four components of the polarizabilities of CH_3NH_2 and $(CH_3)_2NH$ involves use of the bond-additivity model to estimate α_{xy} and, finally, the simultaneous solution of eqs 5b, 6b, and 7.

Bond-Additivity Model

As noted above, the essence of the bond-additivity model implemented here is to use the experimental data for NH_3 and $(CH_3)_3N$ to determine the longitudinal and transverse (L and T) components of the polarizabilities of the axially symmetric N−H and N−CH_3 bonds and then to combine these, in accordance with the molecular geometries and the tensor transformation law, to predict all four components of the polarizability of CH_3NH_2 and, in turn, $(CH_3)_2NH$.

Consider, first, the analysis of the components (α_{xx}, α_{zz}) of the polarizability of, for example, NH_3 to obtain the components (α_L^{NH}, α_T^{NH}) of the polarizability of the N−H bond. As previously mentioned, α is the mean molecular polarizability, and ϕ, the angle between the longitudinal axis of the N−H bond and the z axis, is given by

$$\phi = \arcsin\left[\left(\frac{2}{\sqrt{3}}\right)\sin\left(\frac{\chi}{2}\right)\right] \tag{8}$$

where $\chi = \angle$HNH (Figure 1). From the model,

$$\alpha_L^{NH} - \alpha_T^{NH} = \left(\frac{2}{3}\right)(\alpha_{zz} - \alpha_{xx})/(3\cos^2\phi - 1) \tag{9}$$

and since

$$\alpha_L^{NH} + 2\alpha_T^{NH} = \alpha \tag{10}$$

the required components are immediately accessible. A similar analyis of the polarizability of $(CH_3)_3N$ yields the components of the polarizability of the N−CH_3 bond.

Now consider the synthesis of the four components of the polarizabilities of CH_3NH_2 and $(CH_3)_2NH$ from the components for the constituent bonds. In the case of CH_3NH_2, these emerge as

$$\alpha_{xx} = \alpha_L^{NCH_3} + 2\alpha_L^{NH}\cos^2\psi + 2\alpha_T^{NH}\sin^2\psi \tag{11}$$

$$\alpha_{yy} = \alpha_T^{NCH_3} + 2\alpha_L^{NH}\sin^2\psi\cos^2\xi + 2\alpha_T^{NH}(\cos^2\psi\cos^2\xi + \sin^2\xi) \tag{12}$$

$$\alpha_{zz} = \alpha_T^{NCH_3} + 2\alpha_L^{NH}\sin^2\psi\sin^2\xi + 2\alpha_T^{NH}(\cos^2\psi\sin^2\xi + \cos^2\xi) \tag{13}$$

$$\alpha_{xy} = 2(\alpha_L^{NH} - \alpha_T^{NH})\cos\psi\sin\psi\cos\xi \tag{14}$$

in which $\psi = \angle$ HNC and ξ, the angle between the projection of the N−H bond onto the yz plane and the y axis, is given by

$$\xi = \arcsin\left[\frac{\sin\left(\frac{\chi}{2}\right)}{\sin\psi}\right] \tag{15}$$

where $\chi = \angle$ HNH (Figure 1). The expressions for $(CH_3)_2NH$ are

$$\alpha_{xx} = 2\alpha_L^{NCH_3}\cos^2\left(\frac{\chi}{2}\right) + 2\alpha_T^{NCH_3}\sin^2\left(\frac{\chi}{2}\right) + \alpha_L^{NH}\cos^2\epsilon + \alpha_T^{NH}\sin^2\epsilon \tag{16}$$

$$\alpha_{yy} = 2\alpha_T^{NCH_3} + \alpha_L^{NH}\sin^2\epsilon + \alpha_T^{NH}\cos^2\epsilon \tag{17}$$

$$\alpha_{zz} = 2\alpha_L^{NCH_3}\sin^2\left(\frac{\chi}{2}\right) + 2\alpha_T^{NCH_3}\cos^2\left(\frac{\chi}{2}\right) + \alpha_T^{NH} \tag{18}$$

$$\alpha_{xy} = -(\alpha_L^{NH} - \alpha_T^{NH})\cos\epsilon\sin\epsilon \tag{19}$$

in which $\chi = \angle$ CNC and ϵ, the angle between the longitudinal axis of the N−H bond and the (negative) x axis, is given by

$$\epsilon = \arccos\left[\frac{-\cos\psi}{\cos\left(\frac{\chi}{2}\right)}\right] \tag{20}$$

where $\psi = \angle$ HNC. Note, from eqs 14 and 19, that for both CH_3NH_2 and $(CH_3)_2NH$ the choices of reference axes are such that only the N−H bonds contribute to α_{xy}, the off-diagonal polarizability.

Obviously, if R (eq 5b), κ^2 (eq 6b), and α (eq 7) are known, then the bond-additivity model is required only to estimate the experimentally inaccessible off-diagonal component of the polarizability, but if any one of these three quantities were uncertain or unknown, then the model could also provide an estimate of this quantity. In any event, the predicted values of the diagonal components are of interest, if only in the context of the validation of the model.

Experimental Section

Samples and purities determined by gas chromatography were NH_3 (Matheson) >99.7%, CH_3NH_2 (Aldrich) >99.5%, $(CH_3)_2NH$ (Aldrich) >99.8%, and $(CH_3)_3N$ (Matheson) >99.7%; all were used without further purification.

Improved equipment for measurements of the temperature and pressure dependence of the electrooptical Kerr effect in gases has been described.[8,9] Observations of the field-induced birefringences of NH_3, CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$ at 632.8 nm typically were made at 12 temperatures (∼295−495 K) within the available span and, at each temperature, over a range of pressures (∼40−400 kPa). The definition of the molar Kerr constant, ${}_{m}K$, is[4,10]

$${}_{m}K = 6nV_m[(n^2+2)^2(\epsilon_r+2)^2]^{-1}[(n_X - n_Y)F_X^{-2}]_{F_X=0} \tag{21}$$

where n and ϵ_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, ${}_{m}K$ can be expressed in terms of V_m as

$${}_{m}K = A_K + B_K V_m^{-1} \tag{22}$$

in which A_K and B_K are the Kerr first and second virial coefficients. In practice, the observed birefringences were used to establish values of

$${}_{m}K_0 = \left(\frac{2}{27}\right)V_m(n_X - n_Y)F_X^{-2} \tag{23}$$

and these were fitted to the relation[11]

$${}_{m}K_0 = A_K + \left[B_K + A_K\left(2A_\epsilon + \left(\frac{1}{2}\right)A_R\right)\right]V_m^{-1} \tag{24}$$

in which A_ϵ and A_R are the low-density molar dielectric polarization and refraction calculated from the static and optical-frequency molecular polarizabilities. For NH_3 and CH_3NH_2, reported density second virial coefficients, B, were used to obtain molar volumes from the vapor temperatures and pressures;[12] for $(CH_3)_2NH$, available data[12] were augmented by values calculated by means of a Stockmayer potential ($\epsilon/k = 1026$ K, $\sigma = 0.237$ nm),[13] and for $(CH_3)_3N$, in the absence of alternatives, results[12] for a limited range of temperature were fitted to the function $\log|B| = m \log T + c$, which was found to be adequate for short extrapolations. 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; with calibration and other systematic errors, the overall accuracy is estimated to be ±3%. Under the conditions of the measurements, B_K makes a relatively small contribution to the observed effect, and once again, values of this quantity were much less well determined. The temperature dependence of B_K would be expected to be explicable on the basis of the dipole−induced dipole model of intermolecular collisions,[14,15] but as noted recently in relation to data for CH_3COCH_3,[1] the sensitivity of the calculated values to the choices of force constants and shape factors, on one hand, and the uncertainty in the experimental values, on the other, are likely to obscure the level of agreement, and the matter will not be pursued here.

The vapor-phase Kerr effect of NH_3, under properly defined physical conditions, was measured nearly 80 years ago by Szivessy,[16] who reported a molar Kerr constant, ${}_{m}K$, at 291.0 K, 101.3 kPa, and 589 nm ($\sim 6.8 \times 10^{-27}$ m^5 V^{-2} mol^{-1}) that is only ∼3% higher than the value calculable from the present results($\sim 6.6 \times 10^{-27}$ m^5 V^{-2} mol^{-1}). A wider, although still

TABLE 1: Temperature Dependence of the Vapor-State Kerr Effects of NH_3, CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$ 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})	B_K (10^{-30} m^8 V^{-2} mol^{-2})
			NH_3		
492.1	11	159−408	−70	2.124 ± 0.018	0.66 ± 0.21
483.5	6	102−153	−77	2.21 ± 0.09	
476.6	12	140−404	−83	2.213 ± 0.013	1.32 ± 0.15
449.9	10	142−363	−93	2.541 ± 0.006	1.19 ± 0.07
422.1	11	137−379	−109	2.794 ± 0.031	1.80 ± 0.35
395.8	12	113−335	−127	3.250 ± 0.020	1.86 ± 0.23
375.7	12	133−374	−145	3.686 ± 0.013	1.89 ± 0.13
356.6	14	124−373	−165	4.109 ± 0.009	1.87 ± 0.09
342.9	11	101−322	−182	4.467 ± 0.005	1.99 ± 0.05
330.2	13	96−346	−198	4.845 ± 0.007	2.17 ± 0.07
319.3	13	109−307	−216	5.154 ± 0.008	2.67 ± 0.09
306.8	12	100−319	−246	5.639 ± 0.004	2.73 ± 0.04
297.5	12	91−262	−275	6.030 ± 0.008	2.68 ± 0.09
			CH_3NH_2		
490.5	9	122−215	−147	−0.875 ± 0.023	−1.0 ± 0.5
451.8	9	101−220	−174	−1.265 ± 0.033	1.7 ± 0.7
411.8	7	90−146	−209	−1.467 ± 0.041	−0.9 ± 1.0
387.0	9	93−259	−241	−1.857 ± 0.010	2.8 ± 0.2
364.2	12	91−212	−274	−2.064 ± 0.011	3.0 ± 0.2
348.9	10	86−204	−306	−2.372 ± 0.014	4.6 ± 0.2
331.8	11	80−214	−344	−2.601 ± 0.019	5.9 ± 0.3
312.9	10	76−196	−403	−3.063 ± 0.008	8.1 ± 0.1
305.4	11	66−258	−431	−3.120 ± 0.010	7.5 ± 0.1
297.3	9	80−254	−466	−3.300 ± 0.013	8.4 ± 0.2
			$(CH_3)_2NH$		
498.7	11	74−182	−186	−2.274 ± 0.031	−0.6 ± 0.9
466.5	9	77−175	−216	−2.867 ± 0.024	2.3 ± 0.6
439.0	10	54−175	−252	−3.194 ± 0.024	3.3 ± 0.6
407.5	10	60−176	−303	−3.916 ± 0.034	4.8 ± 0.7
373.3	9	66−166	−391	−4.630 ± 0.010	4.0 ± 0.2
364.0	12	60−170	−406	−5.039 ± 0.016	5.4 ± 0.3
353.2	10	49−158	−450	−5.304 ± 0.010	6.3 ± 0.2
342.3	13	49−150	−478	−5.737 ± 0.017	6.8 ± 0.4
328.4	13	43−140	−524	−6.173 ± 0.013	6.8 ± 0.3
312.6	12	47−161	−595	−6.870 ± 0.010	8.9 ± 0.2
305.2	12	41−118	−643	−7.224 ± 0.021	10.6 ± 0.5
294.4	11	36−109	−717	−7.889 ± 0.012	14.4 ± 0.4
			$(CH_3)_3N$		
490.4	8	65−127	−237	−1.406 ± 0.024	2.2 ± 0.9
469.8	8	74−139	−260	−1.722 ± 0.045	6.9 ± 1.4
446.6	8	80−175	−293	−1.787 ± 0.012	1.5 ± 0.3
427.0	9	62−123	−324	−2.108 ± 0.047	4.3 ± 1.6
405.3	11	57−128	−366	−2.429 ± 0.034	4.4 ± 1.0
386.8	13	66−190	−395	−2.631 ± 0.019	4.7 ± 0.4
367.6	11	48−131	−457	−3.067 ± 0.020	7.1 ± 0.5
347.3	11	46−127	−520	−3.279 ± 0.011	4.7 ± 0.3
326.0	12	41−127	−599	−3.819 ± 0.015	7.5 ± 0.4
312.1	13	40−127	−666	−4.099 ± 0.020	7.4 ± 0.5
308.0	9	42−121	−689	−4.101 ± 0.041	5.4 ± 1.1
295.3	11	40−110	−756	−4.677 ± 0.021	10.3 ± 0.5

[a] Density second virial coefficients.

limited, investigation of the effect in NH_3 was subsequently conducted by Breazeale,[17] but comparisons with his work are less than straightforward. The three amines have not previously been examined. In addition, dilute-solution Kerr constants are on record[18] for NH_3 and $(CH_3)_3N$ 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.[19]

Finally, it is worthy of note here that, in the course of this study, considerable effort was devoted to the measurement of the Rayleigh depolarization ratios of NH_3, CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$. Unfortunately, under the conditions of the experiments, the effects displayed by these weakly anisotropic species were very small, and especially in view of the need for a rigorous exclusion of spurious vibrational Raman contributions, it proved impossible to obtain a consistent set of data of adequate reliability. However, for NH_3 and CH_3NH_2, values of ρ_0 and κ^2 are already on record[3] and, for NH_3 and $(CH_3)_3N$, the molecular symmetry is such that κ^2 is at least as reliably available from the temperature dependence of the Kerr effect and the coefficient R by means of eq 5a. Moreover, in the case of CH_3NH_2, the values of κ^2 ($\times\ 10^{-2}$) obtained from ρ_0 (0.291 ± 0.002) and from the bond-additivity model (0.306), based on reliable values for NH_3 and $(CH_3)_3N$, are in good agreement, so for $(CH_3)_2NH$, reliance on the model seems a justifiable alternative.

Results

Figure 2 displays the experimental data and the fitted plots of A_K against T^{-1}, whereas Table 2 contains the coefficients P,

TABLE 2: Analysis of the Temperature Dependence of A_K of NH_3, CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$ at 632.8 nm[a]

	value			
property	NH_3	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$
$P(10^{-27}\ m^5\ V^{-2}\ mol^{-1})^b$	0.40 ± 0.27	1.9 ± 1.2	0.7 ± 0.9	2.2 ± 1.0
$Q(10^{-24}\ m^5\ V^{-2}\ mol^{-1}\ K)^c$	-0.43 ± 0.20	-1.0 ± 0.8	-0.1 ± 0.6	-1.4 ± 0.7
$R(10^{-21}\ m^5\ V^{-2}\ mol^{-1}\ K^2)^d$	0.626 ± 0.037	-0.15 ± 0.14	-0.71 ± 0.11	-0.19 ± 0.14
$\alpha(10^{-40}\ C\ m^2\ V^{-1})$	2.47 ± 0.02^e	4.46 ± 0.04^e	6.56 ± 0.07^f	8.66 ± 0.09^f
$\alpha^0(10^{-40}\ C\ m^2\ V^{-1})^g$	2.60 ± 0.08	4.67 ± 0.14	6.60 ± 0.20	8.83 ± 0.26
$\kappa^2(10^{-2})$ (from ρ_0)	0.180 ± 0.007^e	0.291 ± 0.002^e		
(from A_K vs T)	0.158 ± 0.018^h			0.039 ± 0.057^h
(from model)		0.306	0.169	
$\mu_x(10^{-30}\ C\ m)$		-1.281 ± 0.014^j	-0.522 ± 0.005^k	
μ_y		4.234 ± 0.048^j	3.332 ± 0.033^k	
μ_z	4.90984 ± 0.00024^i			2.041 ± 0.034^l
$\alpha_{xy}(10^{-40}\ C\ m^2\ V^{-1})$		0.116	0.157	
α_{xx}	2.37 ± 0.02	4.87 ± 0.04^m	6.54 ± 0.23^m	8.83 ± 0.15
α_{yy}	2.37 ± 0.02	4.43 ± 0.07^m	6.12 ± 0.08^m	8.83 ± 0.15
α_{zz}	2.67 ± 0.02	4.08 ± 0.05^m	7.01 ± 0.15^m	8.32 ± 0.26
$\theta(°)^n$		-14	-18	
$\beta^K(10^{-50}\ C\ m^3\ V^{-2})$	-0.2 ± 0.1	-0.6 ± 0.3	-0.1 ± 0.4	-1.7 ± 0.9
$\gamma^K(10^{-60}\ C\ m^4\ V^{-3})$	0.5 ± 0.3	2.2 ± 1.4	0.8 ± 1.0	2.6 ± 1.2

[a] SI units. Relevant conversion factors are α, 1×10^{-40} C m^2 V^{-1} = 6.0651 au = 0.89867×10^{-24} esu; β, 1×10^{-50} C m^3 V^{-2} = 311.88 au = 2.6944×10^{-30} esu; γ, 1×10^{-60} C m^4 V^{-3} = 1.6038×10^4 au = 8.0776×10^{-36} esu. [b] Equation 3. [c] Equation 4. [d] Equation 5; the polarizability anisotropies, $\Delta\alpha = \alpha_{zz} - \alpha_{xx}$ ($\times 10^{-40}$ C m^2 V^{-1}), of NH_3 and $(CH_3)_3N$ are directly calculable from R as 0.294 ± 0.017 and -0.52 ± 0.37, respectively. [e] Reference 3. [f] Calculated as $\alpha = (3\epsilon_0/N_A)_mR$ from molar refractions ($_mR/10^{-6}$ m^3 mol^{-1}), interpolated to 632.8 nm (14.87, 19.64), obtained by summations of atomic, group, and structural refractions given in Table 22 of ref 20; uncertainties are estimated to be ±1%. [g] Reference 21. [h] Equations 5a and 6a. [i] Reference 22. [j] Reference 23. [k] Reference 24. [l] Reference 25. [m] Uncertainty is the sum of the contributions that arise from the uncertainties in R (measured standard deviation, given above), κ^2 (estimated uncertainty of ±5%), and α_{xy} (estimated uncertainty of ±10%). [n] Figure 1; $\theta = (^1/_2)\arctan[2\alpha_{xy}(\alpha_{yy} - \alpha_{xx})^{-1}]$ (see text).

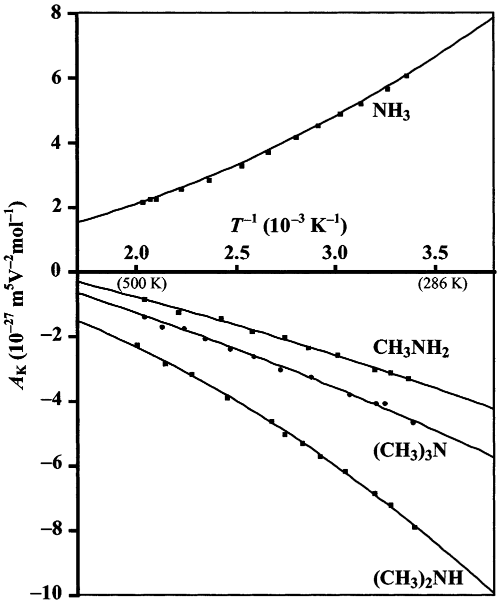

Figure 2. Temperature dependence of A_K of NH_3, CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$.

Q, and R of the polynomials $A_K = P + QT^{-1} + RT^{-2}$ and the interpretation of these in terms of molecular properties. Once again, the temperature range of the measurements is unavoidably limited (to ~200 K), so the precision that can be achieved in the coefficients of a quadratic equation is also limited. For this reason, it has in the past generally been necessary, by whatever approximation is least unsatisfactory, to reduce the quadratic equation to a more manageable linear equation. In the present study, however, standard propagation of errors, to the extent that this is possible, shows that R and the derived polarizabilities are adequately determined, although P and Q and the derived hyperpolarizabilities are less adequately determined. In relation to R, it is immediately obvious, from eq 5a, that since the values for NH_3 and $(CH_3)_3N$ have opposite signs the polarizability anisotropies, $\alpha_{zz} - \alpha$, of these molecules must also have opposite signs.

TABLE 3: N−H and N−CH_3 Bond Polarizabilities from NH_3 and $(CH_3)_3N$ Molecular Polarizabilities

	value	
property	NH_3	$(CH_3)_3N$
$\alpha_{xx}(10^{-40}\ C\ m^2\ V^{-1})$	2.37^a	8.83^a
α_{zz}	2.67^a	8.32^a
$\chi(°)^b$	107.2^c	110.9^c
$\phi(°)^b$	68.4^d	72.0^d
$\alpha_L^{NH}(10^{-40}\ C\ m^2\ V^{-1})$	0.60	
α_T^{NH}	0.93	
$\alpha_L^{NCH_3}$		3.21
$\alpha_T^{NCH_3}$		2.73

[a] Table 2. [b] Figure 1. [c] Reference 26. [d] Equation 8.

TABLE 4: CH_3NH_2 and $(CH_3)_2NH$ Molecular Polarizabilities from N−H and N−CH_3 Bond Polarizabilities

	value	
property	CH_3NH_2	$(CH_3)_2NH$
$\chi(°)$	105.8^a	112.2^a
$\psi(°)$	111.0^a	108.9^a
$\xi(°)$	58.7^b	
$\epsilon(°)$		54.5^c
$\alpha_{xx}(10^{-40}\ C\ m^2\ V^{-1})$	$4.99\ (4.87)^d$	$6.57\ (6.54)^d$
α_{yy}	4.44 (4.43)	6.17 (6.12)
α_{zz}	4.17 (4.08)	7.05 (7.01)
α_{xy}	0.116	0.157
$\kappa^2(10^{-2})^e$	0.306	0.169

[a] Reference 26. [b] Equation 15. [c] Equation 20. [d] Experimental values (Table 2). [e] Equation 6b.

Data in Table 2 that come from other sources are the mean optical-frequency[3,20] and static[21] polarizabilities, α and α^0;

TABLE 5: Contributions to A_K of NH_3, CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$ at 300 K

	value (10^{-27} m^5 V^{-2} mol^{-1})			
term	NH_3	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$
$(N_A/81\epsilon_0)\gamma^K$	0.40 (+6.8%)	1.87 (−57.1%)	0.68 (−9.0%)	2.19 (−49.0%)
$(2N_A/243\epsilon_0 kT)\mu\beta^K$	−1.49 (−25.2%)	−3.71 (+113.2%)	−0.57 (+7.6%)	−4.67 (+104.4%)
$(N_A/45\epsilon_0 kT)\alpha\alpha^0\kappa\kappa^0$	0.04 (+0.7%)	0.22 (−6.7%)	0.27 (−3.6%)	0.11 (−2.4%)
$(N_A/270\epsilon_0 k^2T^2)\mu^2(\alpha_{\mu\mu} - \alpha)$	6.96 (+117.7%)	−1.66 (+50.6%)	−7.92 (+105.0%)	−2.11 (+47.0%)
A_K	5.91	−3.28	−7.54	−4.48

for NH_3 and CH_3NH_2, values of the square of the optical-frequency polarizability parameter, $\kappa^2 = 5\rho_0(3 - 4\rho_0)^{-1}$, derived from previously reported depolarization ratios;[3] and the components μ_x, μ_y, and μ_z of the electric dipole moments.[22−25] In relation to the moments of CH_3NH_2[23] and $(CH_3)_2NH$,[24] Stark-effect measurements have provided the magnitudes but not the signs of the components, so the directions (− to +) of the overall moments have remained speculative. However, the ambiguity is easily removed by recourse to a bond-additivity model that determines the moments of the constituent bonds from the moments of NH_3[22] and $(CH_3)_3N$[25] and then combines these, in conjunction with the molecular geometries, to predict both the magnitudes and the signs of the components of the moments of CH_3NH_2 and $(CH_3)_2NH$. Clearly, the model is similar to, but algebraically much simpler than, that already described for the polarizabilities, and it will not be detailed here. Suffice it to say that the model satisfactorily reproduces the observed moments of CH_3NH_2 and $(CH_3)_2NH$ and in each case resolves the uncertainty associated with the signs of the components and the direction of the overall moment. Of course, the observed values, with the correct signs, are shown in Table 2 and used in the calculations that follow.

The new results, in addition to *P*, *Q*, and *R*, are, for NH_3 and $(CH_3)_3N$, values of κ^2 derived from *R* and α by means of eq 6a; for CH_3NH_2 and $(CH_3)_2NH$, values of κ^2 derived from the bond-additivity model and eq 6b; the two, or four, independent components of $\alpha_{\alpha\beta}$; for CH_3NH_2 and $(CH_3)_2NH$, the angles, $\theta = (^1/_2)\arctan[2\alpha_{xy}(\alpha_{yy} - \alpha_{xx})^{-1}]$,[26] through which the *x* and *y* reference axes must be rotated to locate the x' and y' principal axes; and, for all four species, the hyperpolarizabilities β^K and γ^K.

The use of the bond-additivity model to estimate α_{xx}, α_{yy}, α_{zz}, α_{xy}, and κ^2 for CH_3NH_2 and $(CH_3)_2NH$ is summarized in Tables 3 and 4, which give the relevant bond angles[27] and the derived bond and molecular polarizabilities. In relation to the alternative values of κ^2 ($\times 10^{-2}$) in Table 2, it is of interest to note that for NH_3 the value from *R* and α (0.158 ± 0.018) is close to and probably at least as accurate as that from ρ_0 (0.180 ± 0.007) and that for CH_3NH_2 the prediction of the bond-additivity model (0.306) is close to the experimental result (0.291 ± 0.002).[3] There are, therefore, reasonable grounds to infer that the bond-additivity value for $(CH_3)_2NH$ and the experimental value for $(CH_3)_3N$ are also accurate, although in the latter case very small and rather imprecise.

Finally, Table 5 displays the absolute and percentage contributions of the four terms in eq 1 to the value of A_K at 300 K. Obviously, these contributions are uncertain because the coefficients *P*, *Q*, and *R* are uncertain, but the effects appear to be dominated, in two cases, by the $\mu^2(\alpha_{\mu\mu} - \alpha)$ term (i.e., by the RT^{-2} term in eq 2) and, in the other two cases, by the $\mu\beta^K$ term, with smaller contributions from, in order, the γ^K and $\alpha\alpha^0\kappa\kappa^0$ terms. Note, too, in relation to eq 5b that although α_{xy} is small it may not be small in comparison with $\alpha_{xx} - \alpha$ and $\alpha_{yy} - \alpha$ and that in the reference axis systems the $\mu_x\mu_y\alpha_{xy}$ term may well be an important contributor to A_K, as is certainly the case with CH_3NH_2 (56.1%) and $(CH_3)_2NH$ (10.6%). A brief discussion of the results concludes this report.

Discussion

The main outcomes of this investigation are the development of a novel experimental route to the four independent components of the electric dipole polarizabilities of molecules of C_s symmetry and, by way of demonstration, the specification of the anisotropic polarizabilities at 632.8 nm of NH_3, CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$, for which data have not been available. Because the experimental (Table 2) and bond-additivity calculated (Table 4) values for both CH_3NH_2 and $(CH_3)_2NH$ are in agreement, it follows that the anisotropic polarizabilities, as well as the isotropic polarizabilities, of the four species that comprise the series conform to the simple additivity model that is invoked here. A point that is well illustrated by the present study is that the magnitude and sign of A_K are sensitively dependent on the orientation of the molecular dipole moment relative to the axes of the molecular polarizability. In consequence, knowledge of this direction, from Stark-effect measurements and/or bond-additivity calculations such as those that have been utilized here, is essential for a rigorous analysis of data for species of C_s symmetry. Moreover, the same sensitivity is the main reason that, for these very weakly anisotropic molecules, the four contributions to A_K (Table 5) vary in what might initially be seen to be a random or inexplicable manner. However, the magnitudes and signs of these contributions depend on the magnitudes and signs of the relevant isotropic and anisotropic polarizabilities and hyperpolarizabilities, as well as on the magnitude and orientation of the dipole moment and the temperature. Of course, only the algebraic sum of what may be finely balanced contributions is observable. For these reasons, the present analyses of the Kerr effects and anisotropic polarizabilities of CH_3NH_2 and $(CH_3)_2NH$ can be said to be the most intricate that have been performed to date. Finally, it may be noted that, despite the quality of the experimental data, the Kerr effect once again[9] yields only rather imprecise estimates of the hyperpolarizabilities. In the case of NH_3, values of β ($\times 10^{-50}$ C m^3 V^{-2}) and γ ($\times 10^{-60}$ C m^4 V^{-3}) from the present work (−0.2 ± 0.1, 0.5 ± 0.3) and from measurements of electric field-induced second harmonic generation[28,29] (−0.157 ± 0.003, 0.383 ± 0.007) clearly are consistent, but CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$ have not yet been examined by any other method.

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