

The Rayleigh depolarization ratio and rotational Raman spectrum of water vapor and the polarizability components for the water molecule^{a)}

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(Received 3 August 1977)

This paper describes the observation and computer simulation of the rotational Raman spectrum of water vapor and the measurement of the depolarization ratio for Rayleigh scattering from water vapor, which was found to be $(3.0 \pm 1.4) \times 10^{-4}$. These results were combined with the value of the mean polarizability to calculate the principal polarizability components of the water molecule. At 514.5 nm, they are (in units of 10^{-24} cm^3): $\alpha_{xx} = 1.468 \pm 0.003$, $\alpha_{yy} = 1.415 \pm 0.013$, and $\alpha_{zz} = 1.528 \pm 0.013$, where the x axis is the dipole axis and the y axis is perpendicular to the molecular plane.

INTRODUCTION

Knowledge of the behavior of water in its various forms is basic to our understanding of the many systems in which it participates; such knowledge ultimately depends upon the properties of the isolated water molecule.¹ A property which contributes to many physical phenomena is the molecular polarizability tensor, and, although the mean polarizability of the water molecule is known from vapor phase refractive index studies, the principal components of this tensor have yet to be determined experimentally.

The conventional method of measuring polarizability components is to combine mean polarizability results with those of Kerr effect and/or light scattering depolarization ratio measurements.² For an axially symmetric molecule, there are only two unique polarizability components, so that either Kerr effect or depolarization ratio results may be used with the mean polarizability to obtain the components. However, asymmetric top molecules have three unique polarizability components, and all three experimental results are required in order to determine the components.

In the case of water vapor, no depolarization ratio has been reported because of the experimental problems involved in measuring the weak anisotropic intensity under available sample conditions. Similarly, experimental problems have precluded the measurement of a Kerr constant for water vapor, although liquid results indicate that the polarizability anisotropy is very small.³

Recently, expressions for the Raman intensities for rotational transitions in asymmetric top molecules have been presented.⁴⁻⁶ It is found that the relative intensities of transitions in the spectrum depend on the ratio of two of the irreducible spherical tensor components of the polarizability. The simulation of the observed spectrum thus provides an alternative datum which can be used for determining the polarizability components.⁵

In the present work, the rotational Raman spectrum of water vapor has been experimentally observed and synthetically reproduced in an intensity calculation. Secondly, a method for measuring depolarization ratios

of Rayleigh scattering has been developed which circumvents stray light problems inherent in conventional methods; this was used to measure the depolarization ratio of water vapor. Results of these two measurements were then used with a mean polarizability value from the literature to calculate the principal polarizability components for the water molecule.

EXPERIMENTAL

General

The water vapor spectra were excited using a CRL Model 12 argon ion laser operating at 514.5 nm with 7.5 W power. Initial spectra were also excited with a Spectra Physics Model 164-13 argon ion laser (514.5 nm, 1.5 W). The cylindrical fused silica sample cell had Brewster's angle windows for use with our multipass intensity enhancement device.⁷ The sample temperature was adjusted by wrapping the cell body with heating wire, while the sample vapor pressure was controlled by independently regulating the temperature of a side-arm containing an excess of liquid. The sample temperature was monitored using a thermocouple mounted in a well near the scattering volume; the thermocouple readings were calibrated by replacing the water vapor with nitrogen and determining the sample temperature from the relative intensities of the rotational lines.⁸ Because of the perturbing effect of air currents and the possibility of errors in reproducing the temperature conditions, the sample temperature accuracy is estimated as $\pm 10 \text{ K}$.

The spectra were obtained using Spex Model 14018 and Jarrell-Ash Model 25-100 double monochromators; cooled RCA C31034 photomultipliers were used with both systems. Spectra were recorded on magnetic tape using our computer-based digital data acquisition system, which also controlled the spectrometer drive. Frequency and spectral sensitivity calibrations were applied to each spectrum.

Depolarization ratio

Accurate depolarization ratio measurements for elastically scattered light in gases have been reported by Bridge and Buckingham.⁹ They concluded from an analysis of various sources of error that the most accurate

^{a)}Issued as NRCC No. 16308.

results would be obtained by fixing the plane of polarization of the incident light perpendicular to the scattering plane and analyzing the scattered light. The depolarization ratio measurement then consists of determining the intensities of the scattered components polarized parallel I_{\parallel} and perpendicular I_{\perp} to the polarization vector of the incident light, and forming the ratio $\rho = I_{\perp}/I_{\parallel}$. Stringent measures are still required to minimize the stray light contribution to the results.

In the present case, an additional complication is the requirement that the water vapor sample must be heated in order to obtain a sample density high enough for accurate measurements. The apparatus for controlling the cell temperature causes an increase in the stray light. Thus, a method was sought which could account for the stray light contribution to the measured value.

For the depolarization ratio measurements, it was found that sufficient signal could be obtained using a single pass of the focused laser beam. This served to reduce the light scattered from the Brewster angle windows, which was impossible to eliminate from the inner surface. Also, it appeared that some of this scattered light was internally reflected between the cell wall surfaces to give rise to scattering from the silica walls within the spectrometer aperture. To try to eliminate this effect, a cell was machined from a stainless steel block, with Brewster angle windows for passing the laser irradiation and a plane window for observing the light scattered at 90° . Baffles were used to further reduce stray light. This cell was used to measure the depolarization ratio of nitrogen and fluoroform, as a check on the method, as described below. However, measures necessary to prevent water vapor condensation on the windows when working at elevated temperatures gave rise to excessive stray light within this cell; the water vapor measurement thus had to be made using the silica cell described above.

The usual definition of the depolarization ratio includes the contribution from the depolarized rotational Raman lines as well as the strong polarized line at zero frequency shift.¹⁰ The contribution of the stray light to I_{\perp} , which consists only of light scattered due to the anisotropic part of the scattering tensor, thus can be avoided by estimating its total intensity from the intensity of the rotational structure. This was done by normalizing rotational features in the observed anisotropic spectrum to corresponding features in the calculated spectrum. The total integrated intensity of the calculated spectrum was then scaled by the normalization factor to obtain an estimate of the corrected total I_{\perp} . The stray light contribution to I_{\perp} is then the difference between the observed and corrected values.

Note that this method for measurement of I_{\perp} minimizes experimental errors due to convergence, non-ideal analyzer efficiency, and alignment errors. Each of these causes some of the strong I_{\parallel} at zero frequency shift to "leak" into the observed I_{\perp} . Since I_{\perp} is here estimated independently of its observed intensity at zero frequency shift, these errors are avoided.

In order to estimate the contribution of stray light to

I_{\parallel} , it was assumed that the relative intensity of the polarized stray light components is independent of the sample density. This ratio was estimated by extrapolation to, or measurement at, zero sample pressure, as described for the individual cases below. It was then combined with the stray light contribution to I_{\perp} , determined as described above, to estimate the contribution of stray light to I_{\parallel} . This was then subtracted from the observed intensity in order to obtain the corrected I_{\parallel} . The depolarization ratio was then determined from the ratio of the two corrected intensity values.

Depolarization ratio measurements were made using three to five different sample pressures for the various molecules. Each determination consisted of at least three observations of I_{\parallel} and two of I_{\perp} , obtained alternately. Corrections were made for the pulse pair resolution time of the photon counting detection system.

Special care was taken to insure a realistic error estimation. Estimates at each step were made using statistical or propagation of error calculations; where both of these could be made, the largest estimate was taken. The reported depolarization ratios consist of the weighted averages of the separate determinations for each molecule. The error limits specified are estimates of the standard deviation of the mean.

RESULTS

Depolarization ratio

The accuracy of the method described above was tested by trying to reproduce two depolarization ratios which had previously been reported.⁹

Nitrogen has a relatively strong and well resolved rotational spectrum. Measurements were made for three sample pressures ranging from 400 to 800 mm Hg. The anisotropic spectrum was calculated using rotational constants obtained from the analysis of the high resolution Raman spectrum.¹¹ The normalization factor for the observed and calculated I_{\perp} was determined by averaging the factor determined for six or seven strong anti-Stokes transitions and 10–12 strong Stokes transitions. The ratio of the stray light components was estimated by plotting the ratio of the total observed I_{\parallel} to the stray light contribution to I_{\perp} as a function of sample pressure, and extrapolating to zero pressure. The stray light contribution to I_{\parallel} ranged from 50% to 70% of the total observed intensity. The final result obtained was $(0.96 \pm 0.14) \times 10^{-2}$.

Fluoroform was chosen since it has a very small depolarization ratio.⁹ Measurements were made for five sample pressures ranging from 350 to 820 mm Hg. The calculated spectrum was made using rotational constants given in Ref. 12. The rotational spectrum consists of unresolved wings, with maxima at approximately 20 cm^{-1} on either side of the Rayleigh line, and extending to about $\pm 100 \text{ cm}^{-1}$. The normalizing constant was determined from a least squares fit of the observed digitized spectrum to the calculated spectrum, neglecting the frequency range -7.5 – 7.5 cm^{-1} . Because of the range of relative intensities involved, I_{\parallel} was attenuated using a suitably calibrated neutral density filter. The

TABLE I. Vapor phase depolarization ratio measurement. Comparison with previous results.

Sample	Present results (514.5 nm)	Literature ⁹ (632.8 nm)
N ₂	$(0.96 \pm 0.14) \times 10^{-2}$	$(1.018 \pm 0.005) \times 10^{-2}$
CHF ₃	$(2.67 \pm 0.32) \times 10^{-4}$	$(5.0 \pm 0.5) \times 10^{-4}$
H ₂ O	$(2.99 \pm 0.45) \times 10^{-4}$	

ratio of the stray light components was determined using the same method as for nitrogen. The stray light contribution to I_{\parallel} ranged from 20% to 40% of the total observed intensity. The final result obtained was $(2.67 \pm 0.32) \times 10^{-4}$.

For water vapor, measurements were made for three sample conditions, two at a nominal $\frac{2}{3}$ atm pressure and the third at about $\frac{1}{2}$ atm. For each of these the cell temperature was held constant, with the sidearm temperature varied to adjust the sample pressure. A fourth run was made with the sidearm at room temperature in order to directly measure the ratio of the stray light components. The rotational spectrum was calculated as explained below. The normalization factor for the observed and calculated I_{\perp} were determined by averaging factors determined for eight strong features in the spectrum. As for fluoroform, a neutral density filter was required in measuring I_{\parallel} because of the relative intensities of the two components. The stray light contribution to I_{\parallel} ranged from 80% to 90% of the total observed intensity, due to the necessity of using the silica sample cell for this measurement. The final result obtained was $(2.99 \pm 0.45) \times 10^{-4}$.

The depolarization ratios measured using the present method are collected in Table I and compared with results obtained previously.

The present results are seen to be lower than the literature values, with the fluoroform result significantly so. Previously, a pressure dependent stray light behavior in depolarization ratio measurements was observed; it served to reduce the observed values.⁹ The assumption made here that the stray light polarization is independent of pressure thus may not be strictly valid.

Another explanation of this difference is that in the previous measurements, the total scattered light was analyzed, without isolating the Rayleigh components, and thus vibrational Raman scattering could contribute to those results. From measurements on spherical top molecules, it was estimated that such a contribution might be on the order of 2×10^{-4} .⁹ The agreement between this estimate and the discrepancy between the present and previous results indicates that this is a likely explanation for the difference. However, to allow for the possibility of the pressure dependent stray light effect or other systematic errors in the water vapor measurements, the error estimate will be increased to three times the statistically derived standard deviation. The measured depolarization ratio for water vapor will thus be given as $(2.99 \pm 1.35) \times 10^{-4}$.

Special simulation

A general computer program package has been developed to perform the calculation of rovibrational transition intensities in the isotropic and anisotropic Raman spectra of asymmetric top molecules.⁴ For a totally symmetric transition of a molecule having orthorhombic symmetry, there are two irreducible spherical tensor components of the polarizability tensor which contribute to the anisotropic spectrum, and which connect the same initial and final states.⁴⁻⁶ The matrix elements for these tensor components can interfere constructively or destructively in the expression for the intensity, depending on their relative value and the value of the wavefunction coefficients of the states involved.

The two irreducible spherical tensor components and the equivalent Cartesian component representations are⁴⁻⁶

$$\alpha_0^2 = (2\alpha_{zz} - \alpha_{xx} - \alpha_{yy})/\sqrt{6}, \quad (1a)$$

and

$$\alpha_2^2 + \alpha_{-2}^2 = \alpha_{xx} - \alpha_{yy}. \quad (1b)$$

The polarizability component ratio, which determines the relative calculated intensity, is chosen to be

$$R_{20} = (\alpha_2^2 + \alpha_{-2}^2)/\alpha_0^2. \quad (2)$$

The calculations are carried out using a prolate top principal axis system where the z axis is identified with the least moment of inertia of the molecule, and the y axis with the greatest moment of inertia. Thus, in the case of the water molecule, the x axis is the dipole (C_2) axis, the z axis is the other in-plane axis (parallel to the H-H direction), and the y axis is perpendicular to the molecular plane.

The energies and wavefunctions needed for the intensity calculations are available from analyses of high resolution absorption spectra, and have been kindly provided by Flaud and Camy-Peyret from their recent work.¹³

To simulate the effect of the finite spectral slit width on the calculated spectrum, it was convoluted with a Gaussian slit function having the width indicated in the figures, using a published fast Fourier transform routine.¹⁴

The strong dependence of the anisotropic spectrum on the value of R_{20} is demonstrated in Fig. 1. The most satisfactory agreement with the observed spectrum is found when $R_{20} = 0.75 \pm 0.05$ (Fig. 2), where the error limits indicate values which yield noticeably less satisfactory agreement. The variable background in the observed spectrum is Raman scattering from the walls of the silica cell, excited as described in the experimental section. The extra bands in the observed spectrum at 27, 44, and 84 cm⁻¹ are due to a trace air impurity, which also contributes to a similar extent to water bands in the region up to ca. 120 cm⁻¹. Estimates of the mole fraction of water dimer in the saturated vapor¹⁵ indicate that the dimer concentration under our sample conditions should be less than 1%. Dimers thus should make a negligible contribution to the observed spectrum.

As expected, the observed rotational Raman spectrum can be understood in detail on the basis of the rotational

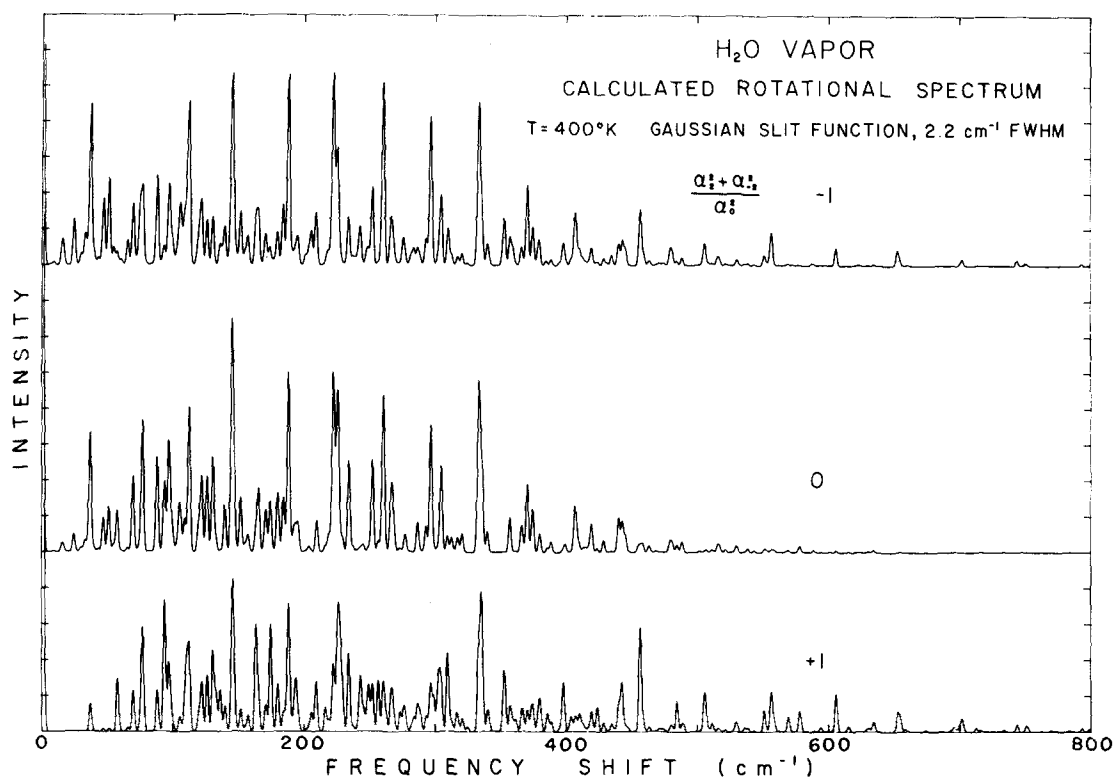


FIG. 1. Dependence of the calculated pure rotational Raman spectrum of water vapor on the ratio R_{20} .

constants derived from the analysis of the high resolution spectrum.¹³ There is thus no need for a detailed analysis or assignment of the observed spectrum; this information may be extracted in a straight forward manner by considering the term values and selection rules.

Polarizability components

The depolarization ratio ρ and the polarizability component ratio R_{20} provide two of the three data needed to determine the principal polarizability components for

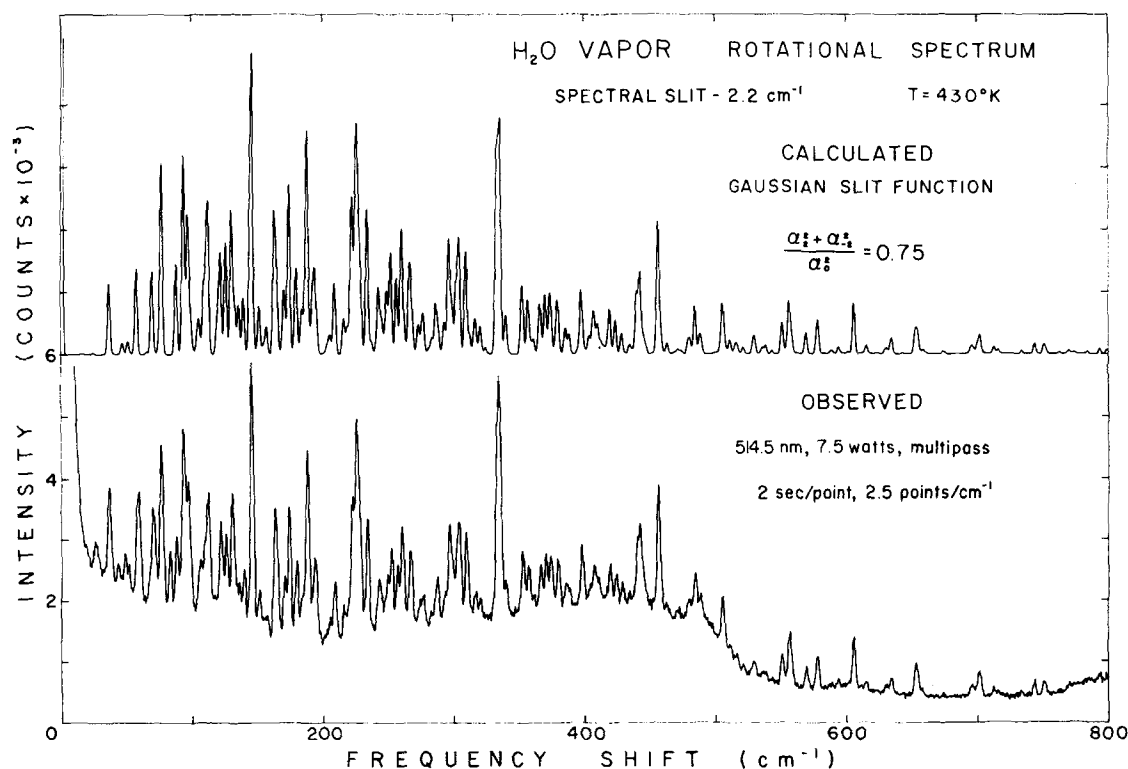


FIG. 2. Pure rotational Raman spectrum of water vapor: comparison of the best calculated spectrum with the observed spectrum.

TABLE II. Polarizability components of water vapor. Included are the principal components and bond components for the two choices of sign for the anisotropy, as well as the calculated error estimates and the correlation coefficients produced in the error calculation. Units for the polarizability components are 10^{-24} cm^3 .

Component ^a	$\beta > 0$	$\beta < 0$	Error	Correlation coefficients		
				α_{xx}	α_{yy}	α_{zz}
α_{xx}	1.4679	1.4727	± 0.0031	1	0.2727	-0.0481
α_{yy}	1.4146	1.5260	± 0.0128		1	-0.9172
α_{zz}	1.5284	1.4122	± 0.0134			1
$\alpha_{ }$	0.7590	0.7112	± 0.0301	$\alpha_{ }$	α_{\perp}	
α_{\perp}	0.7232	0.7471	± 0.0155	1	-0.9100	
					1	

^aThe x axis is the dipole axis and the y axis is perpendicular to the molecular plane.

water vapor. The third datum, the mean polarizability $\bar{\alpha}$ is available from refractive index data.

A literature review has been made of specific refractivity data, and a recommended Cauchy dispersion formula for the specific refractivity, $K(\lambda) = [n(\lambda) - 1]/\rho$, has been given,¹⁶ where n is the refractive index, and, here only, ρ is the vapor density of the sample. This theoretically derived formula provides a very good fit to the accurate relative refractive index measurements,¹⁷ as normalized to the best available absolute refractive index measurements.¹⁸ These latter measurements could be fit to a Cauchy formula with a mean deviation of one part in 600¹⁸; this will be taken as an estimate of the standard deviation of the calculated specific refractivity. Using this formula, a value of $K(514.5 \text{ nm}) = 3.0896 \times 10^{-4} \text{ m}^3/\text{kg}$ is calculated.

The mean polarizability of a vapor is given by the Lorenz-Lorentz equation¹⁹ as

$$\bar{\alpha} = \frac{3}{4\pi N} \frac{n^2 - 1}{n^2 + 2}, \quad (3)$$

where N is the number of molecules per unit volume. Since n is nearly unity, this expression may be simplified and given in terms of the specific refractivity as

$$\bar{\alpha}(\lambda) = MK(\lambda)/(2\pi N_0). \quad (4)$$

Here, M is the molecular weight and N_0 is Avogadro's number. Using the above value of the specific refractivity, one finds $\bar{\alpha}(514.5 \text{ nm}) = (1.4703 \pm 0.0025) \times 10^{-24} \text{ cm}^3$.

For the experimental procedure used here, the depolarization ratio is expressed in terms of the invariants of the polarizability tensor as

$$\rho = 3\beta^2/(45\bar{\alpha}^2 + 4\beta^2). \quad (5)$$

Here, β^2 is the square of the polarizability anisotropy, and $\bar{\alpha}$ and β^2 are defined in terms of the Cartesian components in the usual manner.²⁰ In terms of the nonvanishing irreducible spherical tensor components, β^2 is given as²¹

$$\beta^2 = 3[(\alpha_0^2)^2 + \frac{1}{2}(\alpha_2^2 + \alpha_{-2}^2)^2]/2. \quad (6)$$

These relations have been used with Eqs. (1) and (2) to

calculate the Cartesian tensor components shown in Table II. Since the sign of the anisotropy β is not determined experimentally, two sets of results are found. The error estimates given are derived using propagation of errors considerations²²; the correlation matrix resulting from these calculations is also given.

A choice between the two sets of calculated components may be made by comparison with the results of theoretical calculations of these quantities. Many such calculations have been made; results have been collected and compared.^{23,24} A selection of results which best agree with the experimental value of the mean polarizability is shown in Table III.

A characteristic of all theoretical results is that the out of plane component (y) is the smallest, while the component in the H-H direction (z) is the largest. This is not surprising on an intuitive basis when one considers the ease of inducing polarization along the various molecular axes. This fact compels the choice of the set of experimental components found for positive β as the preferred set.

The agreement between the present results and those calculated in Ref. 25 is extremely good. This method was shown to give excellent agreement with experimental mean polarizabilities for the cases considered; good agreement was also found for the anisotropies where comparison could be made.²⁵ The continual success of this method is evident in the present results. (Although the calculation was made for the static polarizability tensor, while the present result is for the dynamic tensor at 514.5 nm, the small change in the mean polarizability¹⁶ indicates that the individual components probably do not vary appreciably.)

The bond polarizability components³⁰ were calculated from the Cartesian components assuming the bond components to be cylindrically symmetric; the results of the weighted least squares regression calculation are included in Table II. The inverse of the variance-covariance matrix for the Cartesian components was used as the weight matrix,²² and the error limits and correlation coefficient were calculated from the results of the fit using a standard method.²²

The anisotropy of the bond polarizability is involved in the bond polarizability model for vibrational intensities.³¹ For the present case this is found to be $\alpha_{||} - \alpha_{\perp} = +(0.036 \pm 0.045) \times 10^{-24} \text{ cm}^3$; this was used to indicate preferred sets of components of the derived polarizability tensor for ν_2 of water vapor.³²

In the asymmetric top case, the optical anisotropy, as

TABLE III. Principal polarizability components of water vapor. Results of selected theoretical calculations. (Units of 10^{-24} cm^3 , axis system defined in Table II.)

α_{xx}	1.451	1.452	1.519	1.48	1.590
α_{yy}	1.431	1.226	1.221	1.35	1.360
α_{zz}	1.503	1.651	1.696	1.85	1.765
$\bar{\alpha}$	1.461	1.443	1.479	1.56	1.572
Reference	25	26	27	28	29

determined in the Kerr effect, has a value different from that found in a depolarization ratio measurement, since it depends on the direction of the molecular dipole.² For water, this quantity, in terms of the present coordinate system, is $\alpha_{xx} - \frac{1}{2}(\alpha_{yy} + \alpha_{zz})$ and is found to be $(-0.0036 \pm 0.0028) \times 10^{-24} \text{ cm}^3$. Thus, hyperpolarizability contributions should make a major contribution to the Kerr constant of water vapor.²

ACKNOWLEDGMENTS

I wish to thank J. M. Flaud and C. Camy-Peyret for providing wavefunction results from their analysis of the high resolution absorption spectrum. I would also like to acknowledge helpful discussions with H. J. Bernstein and B. J. Orr.

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