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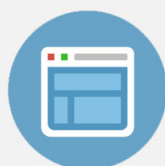
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Rotational Raman intensities and the measured change with internuclear distance of the polarizability anisotropy of H₂, D₂, N₂, O₂, and CO.

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The relative intensities of *O* and *S* branch lines in the $\nu = 1 \leftarrow \nu = 0$ Stokes Raman spectrum of gaseous H₂, D₂, N₂, O₂, and CO have been measured in order to obtain a parameter $\chi = (\alpha_{\parallel} - \alpha_{\perp})_e / \{r_e [\partial(\alpha_{\parallel} - \alpha_{\perp}) / \partial r]_e\}$. Values for χ reflect the detailed molecular electronic structure and are needed in various scattering theories and to correct rotational and vibrational-rotational Raman intensities for molecular nonrigidity and vibrational-rotational interaction. The values of χ obtained are $+0.38 \pm 0.01$ (H₂), $+0.38 \pm 0.01$ (D₂), $+0.45 \pm 0.09$ (N₂), $+0.23 \pm 0.07$ (O₂), and $+0.27 \pm 0.13$ (CO). By combining the measured values of χ with experimental values for $\langle \alpha_{\parallel} - \alpha_{\perp} \rangle_{\nu=0}$ in the literature, the following values of the polarizability anisotropy and its first derivative at r_e are obtained: $(\alpha_{\parallel} - \alpha_{\perp})_e = 0.288$ (H₂), 0.282 (D₂), 0.691 (N₂), 1.080 (O₂), and 0.525 (CO) Å³; $[\partial(\alpha_{\parallel} - \alpha_{\perp}) / \partial r]_e = 1.02$ (H₂), 1.00 (D₂), 1.40 (N₂), 3.89 (O₂), and 1.72 (CO) Å². These values are compared with literature theoretical values.

INTRODUCTION

Molecular polarizability is an experimentally accessible quantity which reflects in a rather direct way the electronic structure of simple molecules. For this reason the orientational anisotropy of molecular polarizability and its variation with internuclear distance are of fundamental interest in developing understanding of the detailed electronic structure of diatomic molecules. Polarizability anisotropies and their derivatives are directly related to both absolute and relative intensities of vibrational and rotational Raman transitions. In this paper we report the values (magnitudes and signs) of a parameter χ which are obtained from measurements of the relative intensities of different vibrational-rotational Raman transitions. The quantity χ is defined¹ as

$$\chi = \beta'_e / r_e \beta'_e \quad (1)$$

where

$$\beta = \alpha_{\parallel} - \alpha_{\perp} \quad (2)$$

is the molecular polarizability anisotropy of the diatomic molecule and

$$\beta'_e = (\partial \beta / \partial r)_e \quad (3)$$

is its first derivative, with r representing the internuclear distance and e indicating the minimum in the interatomic potential. The measurements are based upon the theoretical treatment of James and Klemperer¹ which has recently been extended to overtones by Buckingham and Szabo.² The measured values of χ are combined with literature values of β in $\nu=0$ to extract, to first order, values of β_e and β'_e .

The magnitude of χ determines the degree to which the intensities of pure rotational Raman transitions differ from those of a rigid rotator and the intensities of vibrational-rotational Raman transitions are modified by vibrational-rotational interactions. One specific reason for our interest in this quantity arises from the recent use of the intensities of pure rotational Raman transi-

tions as a temperature and density probe in flames and other reacting high-temperature systems.³⁻⁸ Although molecular nonrigidity is not important when one compares the relative intensities of the low J transitions occurring in pure rotational Raman scattering from a room temperature gas, centrifugal distortion effects become significant at high temperatures, above 1500 K, where for O₂ and N₂ rotational levels up to about $J=40$ are appreciably populated. At 2000 K, neglect of χ when calculating temperatures from pure rotational Raman intensities for O₂ or N₂ leads to errors of about 1% in T .⁷ (For H₂, as has been pointed out previously,^{1,9} the effect of χ on temperature measurements is much larger, about 7% at 2000 K.) The magnitude of χ similarly affects temperature measurements by rotational coherent anti-Stokes Raman spectroscopy,¹⁰ the intensity calibration of spectrometers by measurement of relative rotational Raman intensities,⁹ and rotational temperature measurements by electronic emission or absorption spectroscopy.¹¹

In addition to applications in spectroscopy, experimental values of χ (or β') are needed in calculations of molecular rotational and vibrational excitation upon collision with low energy electrons¹²⁻¹⁶ and for comparison with *ab initio* calculations^{16,17} of molecular polarizabilities as a function of internuclear distance.

In the present work we have determined χ for H₂, D₂, N₂, O₂, and CO by measuring relative intensities of vibrational-rotational transitions in the Stokes Raman spectrum of the room temperature gases. The value of χ is computed from the ratio of the intensities of lines in the *O* and *S* branches which originate from the same initial rotational level J . The variation of polarizability anisotropy with internuclear distance is more important in the intensity of vibrational-rotational transitions than it is in the intensity of pure rotational transitions. Thus, room temperature measurements of *O* and *S* branch intensities yield χ values sufficiently accurate for reliable corrections to high temperature (high J) pure rotational

Raman transitions.

In the following sections we present first the theoretical basis of the measurements, next describe the experimental arrangement, and then present the results.

THEORY

The intensity of a rotational Raman line is described by an equation of the form,¹⁸

$$I = (2\pi\nu/c)^4 I_0 N_{vJ} / (2J+1) \langle \alpha \rangle^2, \quad (4)$$

where I is the energy flux scattered from unit volume per unit solid angle when the direction of propagation of the incident radiation (y), the polarization of the incident radiation (z), and the direction of observation (x) are mutually perpendicular. The symbol ν represents the frequency of the scattered radiation, I_0 is the energy flux density of the (linearly polarized) incident radiation, and N_{vJ} is the number density of molecular scatterers in the initial energy level specified by v and J . Division by $(2J+1)$ accounts for the fact that spectral intensities depend fundamentally upon number densities in the initial state not the initial level.^{8,19}

The squared polarizability matrix element in Eq. (4),

$$\langle \alpha \rangle^2 = \sum_{m_i, m_f} |\langle vJm_i | \alpha_{yz} | v_f J_f m_f \rangle|^2 + \sum_{m_i, m_f} |\langle vJm_i | \alpha_{xx} | v_f J_f m_f \rangle|^2, \quad (5)$$

may be evaluated^{1,2} in the form,

$$\langle \alpha \rangle^2 = C_\beta \cdot S(J) \cdot f(J), \quad (6)$$

where C_β is the intensity factor which depends upon the polarizability of the molecule (assuming a rigid rotator), $S(J)$ is the line strength which describes the J dependence of the intensity arising from the summation over magnetic sublevels and is the same for all rotators (of a given molecular symmetry and electronic state), and f is a correction for vibrational-rotational interaction analogous to the Herman-Wallis factor²⁰ in the infrared.

The line strength for $J_f = J+2$ —pure rotation Stokes scattering and Stokes vibrational-rotational S branches—is (linear molecules in $^1\Sigma$ states)²¹

$$S(J, J+2) = (J+1)(J+2)/(2J+3). \quad (7)$$

As $S(A, B) = S(B, A)$ the line strength for $J_f = J-2$ —anti-Stokes pure rotation and Stokes O branches—is

$$S(J, J-2) = (J-1)J/(2J-1). \quad (8)$$

For pure rotation in $v=0$ where $C_\beta = (7/30)\beta_0^2$, James and Klemperer¹ show that for Stokes scattering,

$$f(J)_{00} = [1 + (4/\chi)(B_e/\omega_e)^2(J^2 + 3J + 3)]^2, \quad (9)$$

where χ is defined by Eq. (1) and the other symbols have their usual spectroscopic meaning. (Because in this paper we take J to represent the initial—as opposed to the lower—level, for pure rotational anti-Stokes scattering, J in Eq. (9) must be replaced by $J-2$).

For Stokes rotational-vibrational scattering¹ where $C_\beta = (7/30)(\tau_e\beta_e')^2(B_e/\omega_e)$, in the S branch,

$$f(J)_{01}^S = [1 - 3(B_e/\omega_e)^2 J(J+1) - 4\chi(B_e/\omega_e)(2J+3)]^2, \quad (10)$$

and in the O branch,

$$f(J)_{01}^O = [1 - 3(B_e/\omega_e)^2 J(J+1) + 4\chi(B_e/\omega_e)(2J-1)]^2. \quad (11)$$

Comparison of Eqs. (10) and (11) with Eq. (9) shows that the correction term in χ goes as B_e/ω_e in the rotational-vibrational spectrum but as $(B_e/\omega_e)^2$ in the pure rotational spectrum which is why χ is more accurately evaluated from relative intensity measurements in O and S branches. There are other differences between pure rotational and vibrational-rotational corrections: in pure rotation the deviation of f from one increases as J^2 and depends inversely upon χ ; in vibration-rotation the deviation of f from one increases as J and depends linearly upon χ .

The measured photon flux I_{meas} is related to the line intensity I of Eq. (4) by

$$I = I_{\text{meas}} \cdot h\nu \cdot R(\nu) / C_{\text{opt}} \quad (12)$$

Multiplication by $h\nu$ converts from photon flux to energy flux. $R(\nu)$ represents the calibrated spectral response of the spectrometer and detection system. The factor C_{opt} , held constant in a given experiment, accounts for the efficiency of the detection system which is determined by the geometry of the collection optics, slit widths, spectrometer f value, phototube characteristics, etc.

To determine χ one compares intensities from the same originating rotational level J in the O and S branches. From Eqs. (4) and (6), if one neglected the f corrections for vibrational-rotational interactions, the ratio $Z^2 = [I^S(J)/S(J, J+2)] \cdot [S(J, J-2)/I^O(J)] \cdot (\nu^O/\nu^S)^4$ would be unity. However, if one considers the intensity modifications arising from vibrational-rotational interactions, one sees that $Z^2 = f^S/f^O$ is less than or greater than one, depending upon whether χ is positive or negative. In terms of experimental quantities, from Eqs. (7), (8), and (12),

$$Z^2 = [I_{\text{meas}}^S(J)/I_{\text{meas}}^O(J)] \cdot [R(\nu^S)/R(\nu^O)] \cdot (\nu^O/\nu^S)^3 \cdot (J-1)J(2J+3)/[(J+1)(J+2)(2J-1)]. \quad (13)$$

From Eqs. (10) and (11), χ can be determined from the measured value of Z using the relationship

$$\chi = a(1 - Z)/[4(2J+3) + 4Z(2J-1)], \quad (14)$$

where

$$a = (\omega_e/B_e) - 3(B_e/\omega_e)J(J+1). \quad (15)$$

Once χ is known, rotational temperatures can be computed from the relative intensities of rotational Raman transitions using the relation⁷

$$\frac{-F_0(J)c_2}{T} = \ln \left(\frac{I_{\text{meas}}(J) \cdot R(\nu)}{f(J) \cdot S(J) \cdot \nu^3 g(J)} \right) + \text{const.}, \quad (16)$$

where $F_0(J)$ is the wave number of level J above $J=0$, c_2 is the second radiation constant, $g(J)$ corrects for nuclear spin symmetry restrictions,⁷ and the other quantities are defined above.

For many purposes, including the calculation of scattering cross sections,¹²⁻¹⁶ it is desirable to break up χ into its components, β_e and β_e' . When the polarizability anisotropy β_0 in $v=0$ is known,²² this can be done by expanding $\beta(\tau)$ in a Taylor series about τ_e ,

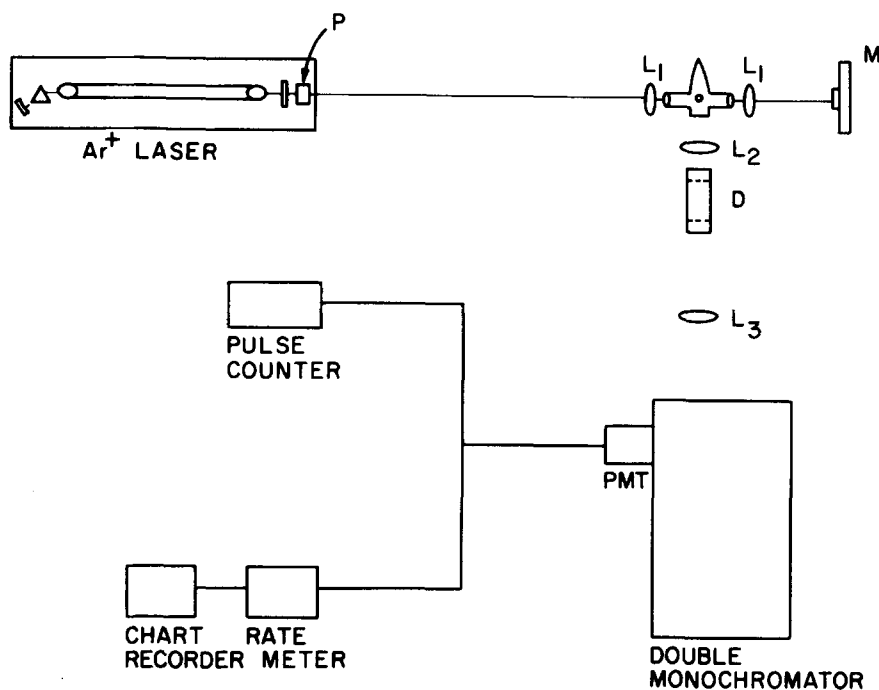


FIG. 1. Schematic diagram of the experimental arrangement: P, power meter used for laser output stabilization; L, lenses; M, mirror; D, dove prism.

$$\beta(r) = \beta_e + \beta'_e(r - r_e) + \frac{1}{2}\beta''_e(r - r_e)^2 + \dots \quad (17)$$

Because the vibrational wave function depends only upon r , the polarizability in vibrational state v is

$$\langle \beta \rangle_v = \langle v | \beta(r) | v \rangle = \beta_e + \beta'_e \langle r - r_e \rangle_v + \frac{1}{2}\beta''_e \langle (r - r_e)^2 \rangle_v + \dots \quad (18)$$

To first order, comparing Eq. (18) with Eq. (1), β_e can be evaluated from $\beta_0 \equiv \langle \beta \rangle_{v=0}$ and χ by the relationship

$$\beta_e = \beta_0 \chi / [(\langle r - r_e \rangle_0 / r_e) + \chi] \quad (19)$$

Once β_e is determined, β'_e can be calculated from χ via Eq. (1).

For H_2 , $\langle r - r_e \rangle_v$ has been calculated to high accuracy by Wolniewicz.²³ For other diatomics, $\langle r - r_e \rangle_v$ can be evaluated in terms of conventional spectroscopic constants by first-order perturbation theory following a procedure similar to that used by Dunham²⁴ and Schlier.²⁵ The result is

$$\langle r - r_e \rangle_v = r_e [(3B_e/\omega_e) + (\alpha_e/2B_e)](v + \frac{1}{2}) \quad (20)$$

where α_e is the vibrational-rotational interaction constant. [Equation (19) is for an anharmonic oscillator. For a harmonic oscillator $\langle r - r_e \rangle_v = 0$ and the first additional term in the expansion of $\langle \beta \rangle_v$, Eq. (18) is the second order term $\frac{1}{2}\beta''_e \langle (r - r_e)^2 \rangle$ with $\langle (r - r_e)^2 \rangle = r_e^2(2B_e/\omega_e) \times (v + \frac{1}{2})$. From Eq. (20),

$$\langle r - r_e \rangle_0 / r_e = (3B_e/2\omega_e) + (\alpha_e/4B_e), \quad (21)$$

which can now be used in Eq. (19).

EXPERIMENTAL

Figure 1 illustrates the experimental arrangement. A Spectra-Physics 171 Ar^+ laser is the excitation source with output power typically adjusted to 2–2.5 W at 4880 Å. The laser beam is reflected back to the laser output mirror with mirror M, creating an external resonator cavity⁷ in which are the sample cell and matched beam focusing lenses L. The external cavity also in-

cludes a beamsplitter so that a portion of the beam is directed to the laser's integral power meter P. In this way the laser power at the sample is increased to 5–6 W while it is stabilized to $\pm 0.5\%$ using a built-in feedback loop which senses the output of the laser power meter.

The sample cell is in the shape of a cross formed by intersection of 2 cm diam and 4 cm diam. Pyrex tubing. The 2 cm glass tube has epoxied Pyrex Brewster angle windows at each end for the vertically polarized focused laser beam. The 4 cm glass tube has an epoxied glass plane window for 90° light collection and a Wood's horn²⁶ opposite the collection window. The body of the cell is painted with opaque colloidal graphite ("Aquadag"). It has provision for attachment to a vacuum system. A chromel-alumel thermocouple is epoxied to the cell.

The 90° scattered light is collected with an overall light-gathering geometry of $f/1.6$ by a 75 mm f.l. camera lens L_2 of $f/1.5$. The light is rotated by a Dove prism and focussed with L_3 , effective $f/8.7$, onto the entrance slit of a Jarrell-Ash 25–100 1 m f.l. double monochromator. The photon flux at the spectrometer exit slit is detected with a thermoelectrically cooled RCA 31034 photomultiplier tube (PMT). (An ITT FW-130 photomultiplier tube was used in the H_2 experiments because of a malfunction in the 31034 tube socket.) For temperature determinations and scanning of gas spectra, spectrometer slits are typically set at 100 μ m, corresponding to a line width (FWHM) of 3.2 cm^{-1} . In these experiments the PMT output is digital-analog converted and amplified by a photon-counting electronics (a rate meter) for presentation on a strip chart recorder. Intensities for temperature determinations are obtained from peak heights.

For χ measurements, where one wishes to compare the relative intensities of O and S branch lines having a common initial rotational level, the spectrometer is not scanned but fixed at the line of interest. Intensities are

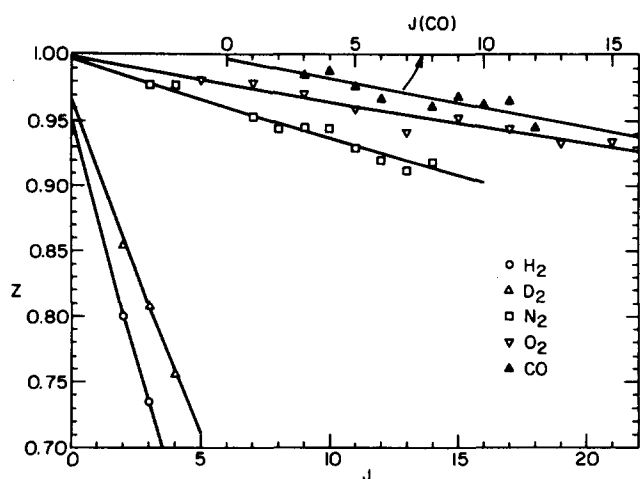


FIG. 2. Experimental values of Z plotted as a function of initial rotational quantum number J . The Z values are obtained from the square root of the ratio of Raman S and O branch line intensities; see Eq. (13). The value of Z measures the degree to which the line intensities are modified by vibrational-rotational interactions; in the absence of such interactions $Z=1$. The lines in the figure are backcalculated from the average χ values obtained from the measurements; see Table I.

measured with an event counter which counts the electrical pulses from the PMT preamplifier that are strong enough to arise from photons incident on the PMT photocathode. For these measurements the spectrometer exit slits are opened to 425 μm , so that the counts are a measure of total peak area. Typically 10 accumulations of 10 sec counts are acquired from a given line and then the spectrometer is reset to measure the intensity of the line originating from the same rotational level in the other vibrational-rotational branch. This procedure maximizes signal-to-noise and minimizes the possibility of errors arising from drifts in cell temperature or laser power. Typical count rates range from 20 sec^{-1} for N_2 , O_2 , and CO to 600 sec^{-1} for H_2 . The background count, about 3 sec^{-1} , is measured for 10 \times 10 sec on each side of each line between determinations and is subtracted.

The wavelength dependence of the spectrometer and detection system is determined using a National Bureau of

TABLE I. Values of $\chi = \beta_e / r_e \beta'_e$.

| | Number of line pairs measured | χ This work | Literature values of χ | |
|--------------|-------------------------------|------------------|-----------------------------|----------------------|
| | | | Experimental | Theoretical |
| H_2 | 2 | $+0.38 \pm 0.01$ | ... | $+0.4,^a +0.378^b$ |
| D_2 | 3 | $+0.38 \pm 0.01$ | $+0.44 \pm 0.08^c$ | Same as H_2 |
| N_2 | 10 | $+0.45 \pm 0.09$ | $\sim 0.4^d$ | $+0.30^e$ |
| O_2 | 9 | $+0.23 \pm 0.07$ | $\sim 0.42^d$ | ... |
| CO | 8 | $+0.27 \pm 0.13$ | ... | ... |

^aCalculated by James and Klemperer (Ref. 1) from results of E. Ishiguro, T. Arai, M. Mizushima, and M. Kotani, Proc. Phys. Soc. London Ser. A 65, 178 (1942).

^bKolos and Wolniewicz, Ref. 17.

^cSmith and Giedt, Ref. 6.

^dMagnitude, but not sign, estimated by James and Klemperer (Ref. 1) from experiments of E. J. Stansbury, M. F. Crawford, and H. L. Welsh, Can. J. Phys. 31, 954 (1953).

^eMorrison and Hay, Ref. 16.

TABLE II. Values of $\beta_e = (\alpha_{||} - \alpha_{\perp})_e$ and $\beta'_e = [\partial(\alpha_{||} - \alpha_{\perp})/\partial r]_e$ calculated from experimental values of β_0 and χ .

| | B_e/ω_e^a | r_e^a (Å) | $\langle r - r_e \rangle_0$ (Å) | β_0^b (Å ³) | β_e (Å ³) | β'_e (Å ²) |
|--------------|------------------------|-------------|---------------------------------|-------------------------------|-----------------------------|------------------------------|
| H_2 | 1.383×10^{-2} | 0.741 | $2.58 \times 10^{-2}^c$ | 0.314 | 0.288 | 1.02 |
| D_2 | 9.762×10^{-3} | 0.741 | 1.73×10^{-2} | 0.299 | 0.282 | 1.00 |
| N_2 | 8.476×10^{-4} | 1.098 | 3.74×10^{-3} | 0.696 | 0.691 | 1.40 |
| O_2 | 9.148×10^{-4} | 1.207 | 4.83×10^{-3} | 1.099 | 1.080 | 3.89 |
| CO | 8.901×10^{-4} | 1.128 | 4.06×10^{-3} | 0.532 | 0.525 | 1.72 |

^aSpectroscopic data tabulated by M. Hizushima, *The Theory of Rotating Diatomic Molecules* (Wiley, New York, 1975).

^bExperimental values of $\beta_0 = \langle \alpha_{||} - \alpha_{\perp} \rangle_{v=0}$ from Bridge and Buckingham, Ref. 22.

^cFrom Wolniewicz, Ref. 23.

Standards traceable, calibrated tungsten strip lamp manufactured by the General Electric Co. Intensity correction factors $R(\nu)$ are obtained by comparing measured intensities with the true intensity emitted by the lamp. The emissivity data of DeVos²⁷ are used to convert brightness temperature to relative radiant intensity as a function of wavelength.

RESULTS

Values of Z computed using Eq. (13) from measured intensities in Stokes O and S branches are plotted as a function of rotational quantum number in Fig. 2. The values of χ computed from these results using Eq. (14) have been averaged and the averages tabulated in Table I. Uncertainties in Table I are two standard deviations which may be a reasonable estimate of the overall uncertainty in the measurements. The lines in Fig. 2 correspond to the χ values in Table I. As Fig. 2 illustrates, even though χ for H_2 and D_2 has a value similar to that for N_2 , the effect on the relative intensities of H_2 and D_2 transitions is much larger because B_e/ω_e for H_2 and D_2 is about an order of magnitude larger than for N_2 (cf. Table II). This causes the χ values measured for H_2 and D_2 to be considerably more precise than those for N_2 , O_2 , and CO .

Figure 3 shows the effect of the rotational-vibrational interaction correction on temperatures calculated from the relative intensities of H_2 ($1 \leftarrow 0$) O and S branch lines. Without correction there are gross discrepancies between O and S branch intensities: the four S -branch points yield 273 K, the two O -branch points yield 309 K, and the combined data (dashed line) yield 300 ± 53 K. The cell temperature measured with the thermocouple is 296 K. After the intensities are corrected for vibrational-rotational interactions the S -branch points yield 296.3 K, the O -branch points yield 296.6 K, and the combined data (unbroken line) yield 296.4 ± 3 K. These H_2 data represent an extreme case. The effect of rotational-vibrational interactions on temperature determinations is much smaller for the nonhydrogenic molecules and also is less significant in pure rotation than in vibration-rotation. The data of Drake and Rosenblatt⁷ illustrate the magnitude of the pure rotational corrections at high temperatures.

DISCUSSION

Table I compares the present values of χ with those determined previously by experiment and theory. With the exception of the theoretical values¹⁷ for H_2 and D_2 , the earlier values are not of high precision. The present measurements are most precise for H_2 and D_2 and it is interesting that the results for hydrogen and deuterium agree with each other and with the calculations of Kolos and Wolniewicz.¹⁷ The theoretical value quoted for N_2 is from a recent calculation¹⁶ which includes electron correlation. Earlier Hartree-Fock calculations by these same authors yield $\chi = 0.31$ for N_2 .

Table II shows the results of combining the present χ values with the measured polarizability anisotropies $\beta_0 = \langle \alpha_{11} - \alpha_{11} \rangle_{v=0}$ of Bridge and Buckingham²² which are tabulated in the fourth column. The values of $\beta_e = \langle \alpha_{11} - \alpha_{11} \rangle_e$ and $\beta'_e = [\partial(\alpha_{11} - \alpha_{11})/\partial r]_e$ in the last two columns have been calculated using Eqs. (1) and (19) along with χ , β_0 , and the values of r_e and $\langle r - r_e \rangle_{v=0}$ shown in the table. The value of $\langle r - r_e \rangle_0$ for H_2 is from the theoretical calculations of Wolniewicz.²³ The other values of $\langle r - r_e \rangle_0$ have been computed using Eq. (20) and spectroscopic constants tabulated by Mizushima.²⁸ The values of β_e are essentially determined by Bridge and Buckingham's measurements of β_0 while the values of β'_e are derived from the present measurements of χ .

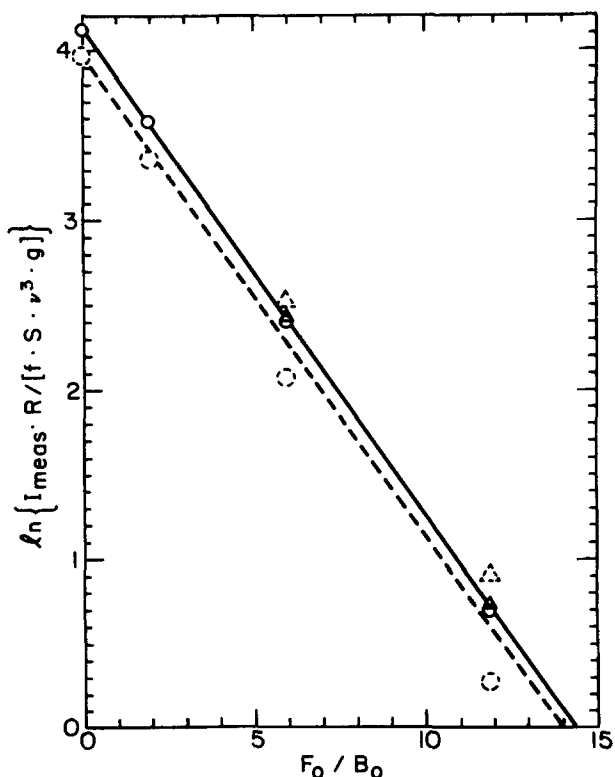


FIG. 3. Determination of rotational temperatures from measured H_2 Stokes (1-0) vibrational-rotational Raman intensities. The ordinate is defined by Eq. (16) of the text and is in arbitrary units; the abscissa $F_0/B_0 \approx J(J+1)$; the slopes of the lines equal $-c_2 B_0/T$. The dashed points and line represent intensities uncorrected for vibrational-rotational interactions: $T = 300 \pm 53$ K. The closed points and solid line represent the same data after correction: $T = 296 \pm 3$ K. The cell temperature measured with a thermocouple is 296 K. Δ , O-branch; \circ S-branch.

TABLE III. Comparison of theoretical and experimental polarizability anisotropies, and derivatives (angstrom units).

| | | | β_0 | β_e | β'_e | β''_e |
|-------|--------|-----------------------|-----------|-----------|------------|-------------|
| H_2 | Theory | (static) ^a | 0.300 | 0.267 | 0.954 | 1.965 |
| | | (6328 Å) ^b | 0.309 | 0.275 | 0.990 | |
| | Expt. | (6328 Å) ^c | 0.314 | 0.288 | 1.02 | ... |
| D_2 | Theory | (static) ^a | 0.290 | 0.267 | 0.954 | 1.965 |
| | | (6328 Å) ^b | 0.299 | 0.275 | 0.990 | |
| | Expt. | (6328 Å) ^c | 0.299 | 0.282 | 1.00 | ... |
| N_2 | Theory | (static) ^d | 0.572 | 0.567 | 1.735 | Small |
| | Expt. | (6328 Å) ^c | 0.696 | 0.691 | 1.40 | ... |

^aKolos and Wolniewicz, Ref. 17.

^bEstimated from static results of Kolos and Wolniewicz using frequency dependencies of Adamov and Evarestov, Ref. 29.

^cFrom Table II.

^dGeneralized valence bond calculation of Morrison and Hay, Ref. 16.

Looking first at N_2 , O_2 , and CO the uncertainties in β'_e are about the same as those in χ : $\pm 20\%$ for N_2 , $\pm 30\%$ for O_2 , and $\pm 50\%$ for CO. However, the uncertainties in β_e arising from uncertainties in χ or in $\langle r - r_e \rangle_0$ are negligible ($< 0.5\%$). Thus, the tabulated values of β_e are of the same accuracy as the experimental values²² of β_0 , about $\pm 2\%$.

For H_2 (and to a lesser extent D_2) the situation is more complicated. This is because terms beyond β'_e have been neglected in the computation of β_e and β'_e from the experimental values of χ and β_0 . The effect of higher-order terms is illustrated by comparison of the experimental values with theoretical results (Table III).

When comparing theory and experiment it has to be remembered that the calculations are for static fields while the measurements are at optical frequencies. Adamov and Evarestov²⁹ present theoretical formulae for the frequency dependencies of α_{11} , α_{11} , $\partial\alpha_{11}/\partial r$, and $\partial\alpha_{11}/\partial r$ for H_2 which yield $\beta_e(6328 \text{ Å})/\beta_e(\text{static}) = 1.029$ and $\beta'_e(6328 \text{ Å})/\beta'_e(\text{static}) = 1.038$. Values of χ calculated from their equations are essentially independent of frequency; χ at 6328 Å is only 0.3% greater than at 4880 Å and 1.1% less than the static value. Adamov and Evarestov's formulae imply, therefore, that the experimental values of β_e and β'_e in Table II are 6328 Å values, that being the wavelength at which β_0 was measured.²² In order to estimate theoretical 6328 Å values for H_2 to compare with the experimental ones (see Table III), the static values of β_e and β'_e derived from the results of Kolos and Wolniewicz have been multiplied by 1.029 and 1.038, respectively.

Tables I and III show that, for H_2 and D_2 , experimental and theoretical values of both χ and β_0 (6328 Å) agree to well within the experimental uncertainties of about $\pm 2\%$. However, the experimentally derived value of β_e for H_2 is 5% (3% for D_2) higher than the theoretical 6328 Å value. The reason for this lies in the high theoretical value of the second derivative $\beta''_e = [\partial^2(\alpha_{11} - \alpha_{11})/\partial r^2]_e$. Because β''_e is large, the second term in the Taylor expansion, Eq. (18), is not negligible. The β''_e term in Eq. (18) contributes 3% (2% for D_2) to the theoretical static value of β_0 for H_2 . For comparison, the

β'_e term contributes 9% (6% for D_2) and the β''_e term $\sim 0.1\%$ to the value of β_0 for H_2 .

Because of this large contribution from β''_e , the 6328 Å theoretical estimates of β_e and β'_e for H_2 and D_2 (Table III) may be preferable to the experimental numbers which were calculated assuming β''_e negligible. The large contribution from β''_e also suggests that first order intensity corrections are not sufficient to describe accurately the pure rotational Raman intensities of the higher J (up to $J=9$) H_2 levels populated in 2000 K flames. This may explain the inaccuracy of H_2 rotational Raman thermometry compared to N_2 rotational Raman thermometry in high-temperature flames.^{7,8}

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