systems using temperature-dependent averages.

The numerical results of the three methods are not very much different for inner-shell orbital energies, total energies, and wave functions. There is a distinct difference in the description of the ground-state configuration obtained from the three methods applied to transition metals. The energy average $\langle H\rangle_N$ has its minimum for the configuration $3d^q 4s^2$ for the four atoms Cr, Fe, Co, and Ni that have been studied here, while the average $\langle H\rangle$ has its minimum for $3d^{q+2}$, and the hyper-Hartree-Fock method points towards an intermediate situation. We feel that wave functions obtained from Eq. (45) and the corresponding potential functions are those best suited for molecular or solid-state applications since the treatment of Coulomb and exchange terms is here similar to the ones used in a tight-binding formulation of the Hartree-Fock method for a molecule or crystal. The valence-shell orbitals are in this case somewhat more diffuse than those obtained by the other procedures and it is necessary to subject this point to a careful analysis with regard to possible "overlap catastrophies."

The connection between the electronegativity concept and the valence-shell orbital energy as defined by Eq. (51) is a satisfying feature of the Hartree-Fock procedure based on ensemble averages without restriction to fixed number of electrons. A further study of the significance of this relation for the discussion of chemical bonding and molecular electronic structure is needed.

ACKNOWLEDGMENTS

The calculations in this paper have been carried out by means of a program originated by Dr. C. Froese-Fischer and we gratefully acknowledge her willingness to make it available. Two of us (Jan Linderberg and Yngve Öhrn) have benefited from discussions on these matters with Professor J. C. Slater and Dr. T. M. Wilson.

---

*Sponsored by NATO under Grant No. 462.

†Present address: Departments of Chemistry and Physics, University of Florida, Gainesville, Fla. 32601.

[1] J. C. Slater, J. B. Mann, T. M. Wilson, and J. H. Wood, Phys. Rev. 184, 672 (1969).

[2] See, e.g., E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge, U. P., Cambridge, England, 1953), p. 335.

[3] J. C. Slater, Phys. Rev. 34, 1293 (1929).

[4] D. R. Hartree, Proc. Cambridge Phil. Soc. 24, 89 (1928).

[5] R. K. Nesbet, Proc. Roy. Soc. (London) A230, 312 (1955); Rev. Mod. Phys. 33, 28 (1961).

[6] L. Brillouin, Actualites Sci. Ind. 71, 1 (1933).

[7] J. C. Slater, Intern. J. Quantum Chem. 3S, 727 (1970).

[8] W. Moffitt, Proc. Roy. Soc. (London) A210, 245 (1951).

[9] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill, New York, 1960), Vol. I., p. 217.

[10] T. Koopmans, Physica 1, 104 (1933).

[11] L. D. Landau, Zh. Eksperim. i Teor. Fiz. 30, 1058 (1956); 32, 59 (1957) [Sov. Phys. JETP 3, 920 (1956); 5, 102 (1957)].

[12] C. K. Jørgensen, *Orbitals in Atoms and Molecules* (Academic, London, 1962), p. 85.

[13] R. S. Mulliken, J. Chem. Phys. 2, 782 (1934).

PHYSICAL REVIEW A VOLUME 6, NUMBER 3 SEPTEMBER 1972

Molecular-Beam Magnetic-Resonance Measurements of the Anisotropies of the Electric Polarizabilities of H_2 and D_2[†]

K. B. MacAdam[*] and N. F. Ramsey
Lyman Laboratory of Physics, Harvard University, Cambridge, Massachusetts 02138

(Received 20 April 1972)

The anisotropies $\gamma = \alpha_{\parallel} - \alpha_{\perp}$ of the static electric polarizabilities of H_2 and D_2 were measured in a molecular-beam magnetic-resonance experiment. The quadratic Stark shifts of the separated-oscillatory-field resonances in the ground electronic and vibrational and $J = 1$ rotational states were measured in parallel electric and magnetic fields. The results are $\gamma(H_2) = 0.3016 \pm .0005$ Å^3 and $\gamma(D_2) = 0.2917 \pm .0004$ Å^3, which agree very closely with theory. A previously measured combination of the spin-rotation and quadrupole-interaction constants of D_2 was independently remeasured, and the dependence upon orientation of the nuclear magnetic shielding of D_2 was found to be $\sigma_{\pm 1} - \sigma_0 = -11 \pm 9$ ppm. An efficient electron-bombardment detector was constructed for this experiment.

I. INTRODUCTION

We report here the first direct measurement of the anisotropy of the static polarizability of H_2 and an improved measurement for D_2, each in the ground electronic and vibrational state and the $J = 1$ rotational state. The method is basically that used by English and MacAdam,[1] namely, the measurement of Stark shifts in the molecular-beam magnetic-resonance spectra. Several modifications, including the use of separated oscillatory fields and the construction of an electron-bombardment detector of high efficiency, have allowed an improvement in the accuracy by an order of magnitude. We also give results for the orientation dependence of the nuclear magnetic shielding of D_2.[2,3]

Accurate measurements of the electric polarizability tensor of molecular hydrogen are of interest to both experimentalists and theoreticians. Hydrogen is often used as a model problem for testing various methods of calculating molecular properties. Subsequent to the accurate variational calculations of Kołos and Wolniewicz,[4] many authors have published theoretical results for the tensor components of the polarizability in the electronic ground state for the equilibrium internuclear separation, $R = 1.4a_0$, where a_0 is the Bohr radius.[5-18] Recently Dalgarno, Ford, and Browne[19] have calculated *ab initio* a rather complete set of dipole oscillator strengths for H_2 from which they have deduced the frequency-dependent tensor polarizability with excellent accuracy. Their results and those of Kołos and Wolniewicz allow for vibrational and rotational motion.

The tensor polarizability of hydrogen is important for the calibration of Raman intensities,[20,21] for the analysis of electric-field-induced[22,23] and pressure-induced[24] spectra, and for the calculation of orientation-dependent van der Waals forces.[25-27] The anisotropy of the polarizability has been measured previously through the Rayleigh depolarization ratio at 6328 and at 4880 Å.[28,29] An indirect measurement of the anisotropy of the static polarizability of H_2 in the $J = 1$ state was made in a molecular-beam E-H gradient-balance experiment.[30] The first direct measurement of the static anisotropy for D_2 was made by the molecular-beam magnetic-resonance technique in a previous experiment in our laboratory.[1,31]

Section II discusses the Hamiltonian for H_2 and D_2 and describes the Stark shifts to be observed in the molecular-beam resonances. Section III describes the apparatus and the experimental conditions. The results are discussed in Sec. IV and are compared with those of other workers in Sec. V.

II. THEORY

The Hamiltonian $\mathcal{H}_0$ for ground state H_2 and D_2 in magnetic fields has been given by Ramsey.[32] The interaction of a uniform external electric field with the molecule can be given in lowest order as an additional term due to the electric polarizability,

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_E^{(2)} , \tag{1}$$

where

$$\mathcal{H}_E^{(2)} = -\tfrac{1}{2} \sum_{ij} E_i \alpha_{ij} E_j \tag{2}$$

for $i, j = x, y, z$, and α_{ij} is the usual molecular elecelectric polarizability tensor. The tensor is diagonal when expressed relative to a coordinate system in which $\hat{z}$ lies along the internuclear axis. In this case, $\alpha_x = \alpha_y \equiv \alpha_\perp$ and $\alpha_z \equiv \alpha_\parallel$. $\mathcal{H}_E^{(2)}$ can be written as the sum of $\mathcal{H}_{E0}^{(2)}$, which transforms as a scalar under rotations, and $\mathcal{H}_{E2}^{(2)}$ which transforms as a spherical tensor of rank two:

$$\mathcal{H}_{E0}^{(2)} = -\tfrac{1}{2} \alpha E^2 , \tag{3}$$

where $\alpha \equiv \frac{1}{3}(2\alpha_\perp + \alpha_\parallel)$, and

$$\mathcal{H}_{E2}^{(2)} = -\tfrac{1}{3} \gamma E^2 C_0^{(2)}(\omega, \nu) , \tag{4}$$

where $\gamma \equiv \alpha_\parallel - \alpha_\perp$. Here $C_q^{(k)}(\omega, \nu)$ is a tensor of rank k and projection q, proportional to the spherical harmonic $Y_{kq}(\omega, \nu)$.[33] Angles (ω, ν) locate the electric field in the molecular-coordinate system. Since the electric field in practice is defined in laboratory coordinates in which the z axis lies along the magnetic field, it is appropriate to transform $\mathcal{H}_{E2}^{(2)}$ to laboratory angles. The addition theorem for spherical harmonics implies that

$$C_0^{(2)}(\omega, \nu) = \textstyle\sum_q (-1)^q C_{-q}^{(2)}(\theta, \phi)\, C_q^{(2)}(\theta_E, \phi_E) , \tag{5}$$

where (θ, ϕ) locates the internuclear axis and (θ_E, ϕ_E) locates the electric field in the laboratory coordinates. The matrix elements of $\mathcal{H}_E^{(2)}$ can be calculated in the $I = J = 1$ state using the uncoupled representation $|I m_I J m_J\rangle$ by standard techniques.[33] $\mathcal{H}_{E0}^{(2)}$ is diagonal and serves only to lower all energies in the $I = J = 1$ state by $\frac{1}{2}\alpha E^2$. Since the transitions of interest are confined to this state, $\mathcal{H}_{E0}^{(2)}$ can be neglected. The matrix elements of $\mathcal{H}_{E2}^{(2)}$ are

$$\langle I m_I' J' m_J' | \mathcal{H}_{E2}^{(2)} | I m_I J m_J \rangle = -\tfrac{1}{3} \gamma E^2 \times \textstyle\sum_q (-1)^{q+m_J'+J} C_q^{(2)}(\theta_E, \phi_E) [(2J'+1)(2J+1)]^{1/2} \times \begin{pmatrix} J' & 2 & J \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} J' & 2 & J \\ -m_J' & -q & m_J \end{pmatrix} \delta_{m_I m_I'} . \tag{6}$$

The matrix elements vanish for $J = 1$ unless $J' = 1$ or 3. The laboratory axes can be defined so that $\phi_E = 0$. The matrix for $I = J = J' = 1$ is given in Fig. 1 in terms of A, B, and C, which are defined by

$$A = \tfrac{1}{15} \gamma E^2 C_0^{(2)}(\theta_E, 0) , \tag{7}$$

$$B = \tfrac{1}{15} \gamma E^2 C_1^{(2)}(\theta_E, 0) , \tag{8}$$

$$C = \tfrac{1}{15} \gamma E^2 C_2^{(2)}(\theta_E, 0) . \tag{9}$$

When the electric and magnetic fields are parallel ($\theta_E = 0$), then $B = C = 0$ and $A = \frac{1}{15}\gamma E^2$, and the matrix of $\mathcal{H}_{E2}^{(2)}$ becomes diagonal. For magnetic fields above about 500 G, the uncoupled basis states constitute the energy eigenstates to a good approxi-

I = J = 1

$$\begin{array}{c|ccccccccc}
m_I' & 1 & 1 & 0 & 1 & 0 & -1 & 0 & -1 & -1 \\
m_J' & 1 & 0 & 1 & -1 & 0 & 1 & -1 & 0 & -1 \\
m_I\ m_J\ M \backslash M' & 2 & 1 & 1 & 0 & 0 & 0 & -1 & -1 & -2 \\
\hline
1\ 1\ 2 & A & -\sqrt{3}B & & \sqrt{6}C & & & & & \\
1\ 0\ 1 & -\sqrt{3}B & -2A & & \sqrt{3}B & & & & & \\
0\ 1\ 1 & & & A & & -\sqrt{3}B & & \sqrt{6}C & & \\
1\ {-1}\ 0 & \sqrt{6}C & \sqrt{3}B & & A & & & & & \\
0\ 0\ 0 & & & -\sqrt{3}B & & -2A & & \sqrt{3}B & & \\
-1\ 1\ 0 & & & & & & A & & -\sqrt{3}B & \sqrt{6}C \\
0\ {-1}\ {-1} & & & \sqrt{6}C & & \sqrt{3}B & & A & & \\
-1\ 0\ {-1} & & & & & & -\sqrt{3}B & & -2A & \sqrt{3}B \\
-1\ {-1}\ {-2} & & & & & & \sqrt{6}C & & \sqrt{3}B & A
\end{array} = \left(\mathcal{H}^{(2)}_{E2}\right)$$

FIG. 1. Nonzero matrix elements of $\mathcal{H}^{(2)}_{E2}$ for H_2 and D_2 in the $I=J=1$ states. The nonzero matrix elements of $\mathcal{H}_0$ are confined to the diagonal blocks marked by bold lines. The quantities A, B, and C are defined in the text.

mation. Therefore the approximate effect of the electric field is to raise the ($m_J = \pm 1$) states in energy by $\frac{1}{15}\gamma E^2$ and to lower the ($m_J = 0$) states by

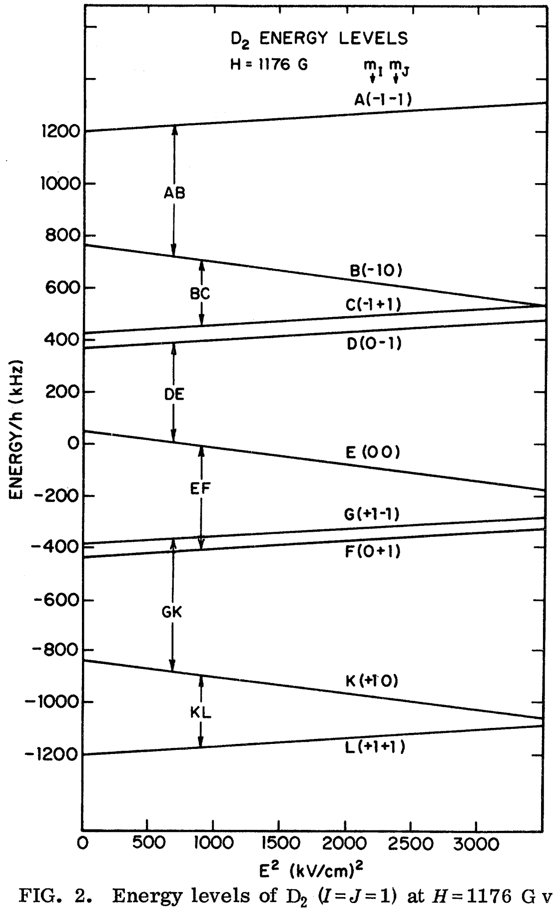

FIG. 2. Energy levels of D_2 ($I=J=1$) at $H=1176$ G vs electric field with $\theta_E = 0$. The levels of H_2 exhibit similar behavior.

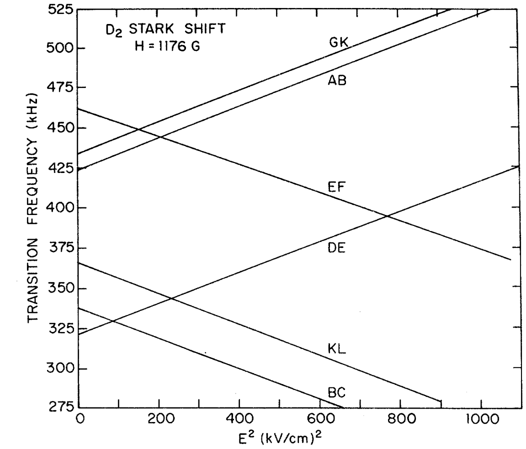

FIG. 3. Stark shifts of the D_2 rotational resonances at $H=1176$ G. "*EF*" refers to the transition between levels *E* and *F*, etc.

$\frac{2}{15}\gamma E^2$. Therefore, the molecular-beam magnetic-resonance transitions corresponding to reorientations of the rotational angular momentum ($\Delta m_J = \pm 1$, $\Delta m_I = 0$) shift up or down in frequency by $\gamma E^2/5h$. Measurement of these quadratic Stark shifts provides a direct measure of $\gamma = \alpha_\parallel - \alpha_\perp$. Figure 2 shows the energy levels of D_2 ($I = J = 1$) in an electric field and their conventional designations.[32] Figure 3 shows the quadratic Stark shifts of the six rotational transitions in D_2. The Stark shifts in H_2 are shown in Fig. 4.

An accurate analysis of the data requires a numerical diagonalization of the 9×9 matrix of $\mathcal{H}_0 + \mathcal{H}^{(2)}_{E2}$ for each value of E and H because the fields determine the exact content of the eigenstates in terms of the basis states. At a fixed magnetic field, the Stark shift contains fourth and higher even powers of E because of the off-diagonal elements of $\mathcal{H}_0$. For the same reason, the Stark shifts become less than $\gamma E^2/5h$ as the magnetic field is reduced from very large values as shown in Fig. 5. The physical reason for this is that in intermediate magnetic fields the rotational transitions are less purely reorientations of the molecular frame and tend to mix instead with nuclear spin reorientations. At intermediate magnetic fields the nuclear transitions ($\Delta m_J = 0$), ($\Delta m_I = \pm 1$) exhibit a small Stark shift but only to the extent that the relatively small off-diagonal elements of $\mathcal{H}_0$ mix basis states.

$\mathcal{H}^{(2)}_{E2}$ has nonzero matrix elements between $J = 1$ and $J' = 3$. However, because of the large spacing of rotational levels in H_2 and D_2, the effect on the Stark shifts is completely negligible at the electric fields used in these experiments. For sufficiently strong electric fields, $\mathcal{H}$ should also include a term

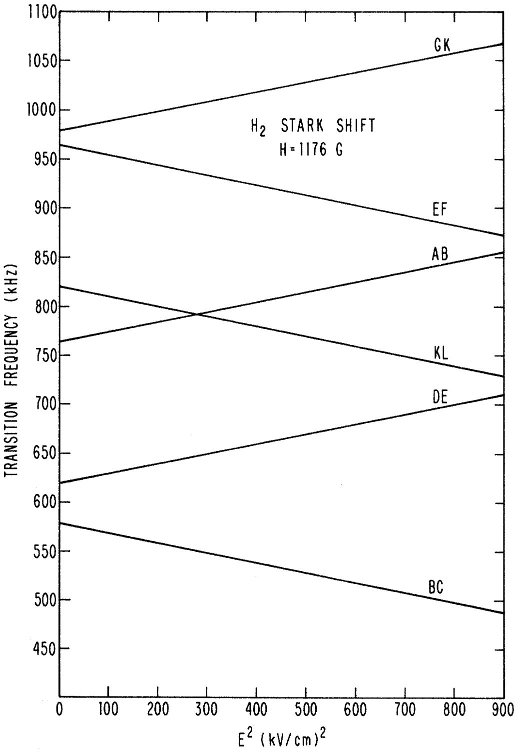

FIG. 4. Stark shifts of the rotational resonances in H_2 at $H=1176$ G.

$$\mathcal{H}_E^{(4)} = -\tfrac{1}{24}\sum_{ijkl} E_i E_j E_k E_l \gamma_{ijkl} , \tag{10}$$

where γ_{ijkl} is known as the second hyperpolarizability tensor. The hyperpolarizability could affect the Stark shifts only through the component term

$$\mathcal{H}_{E2}^{(4)} = -\tfrac{1}{24}\gamma_2 E^4 C_0^{(2)}(\omega, \nu) , \tag{11}$$

where

$$\gamma_2 \equiv \tfrac{1}{21}(12\gamma_\parallel + 4\gamma' - 16\gamma_\perp) . \tag{12}$$

Here $\gamma_\parallel \equiv \gamma_{zzzz}$, $\gamma_\perp \equiv \gamma_{xxxx} = \gamma_{yyyy} = 3\gamma_{xxyy}$, and $\gamma' \equiv 3\gamma_{xxzz} = 3\gamma_{yyzz}$.[34] The average hyperpolarizability of H_2 has been measured by Buckingham and Orr[35] who obtained

$$\gamma_0 = \tfrac{1}{15}(3\gamma_\parallel + 4\gamma' + 8\gamma_\perp) = (0.28 \pm 0.03)\times 10^{-36} \text{ esu} .$$

If the anisotropy γ_2 is of the same order as γ_0, electric fields of 3×10^7 V/cm would be required for the hyperpolarizability to produce 0.1% of the total Stark shift. Therefore the hyperpolarizability can be neglected in these experiments.

III. APPARATUS

The experiments were performed on a magnetic-resonance molecular-beam apparatus described elsewhere.[36,37] The effusive source, which produced beams of H_2 and D_2 at 21–24 K, has been described by Code and Ramsey.[38] The electron-bombardment detector formerly used was replaced by a new one of the type first described by Weiss[39] and successfully adapted by many other workers. The Weiss-type ionizer was followed by a 45° magnetic sector mass spectrometer and an 18-stage electron multiplier, and these formed a detector of excellent sensitivity and versatility.

The efficiency of the ionizer was measured with a D_2 beam at 296 K. The cross section σ for electron-bombardment ionization was assumed to be 9.1×10^{-17} cm², its value for 110-eV electrons.[40] Allowing for the velocity dependence of the ionization probability for molecules passing through the ionizer, the expected ionization efficiency for the D_2 beam was

$$P = \frac{(J/e)\sigma l \pi^{1/2}}{(2\beta)} = 4.92\times 10^{-3} , \tag{13}$$

where $J = 150$ mA/cm² is the anode current density, $l = 7.2$ cm is the length of the ionization region, and $\beta \equiv (2kT/M)^{1/2}$. The mass of the D_2 molecule is M and the beam temperature is T. A direct measurement of the D_2^+-ion output showed that 25% more ions than expected were produced. However, the over-all efficiency for ionizing, focusing, mass selecting, and collecting D_2^+ ions at the first dynode of the electron multiplier was only

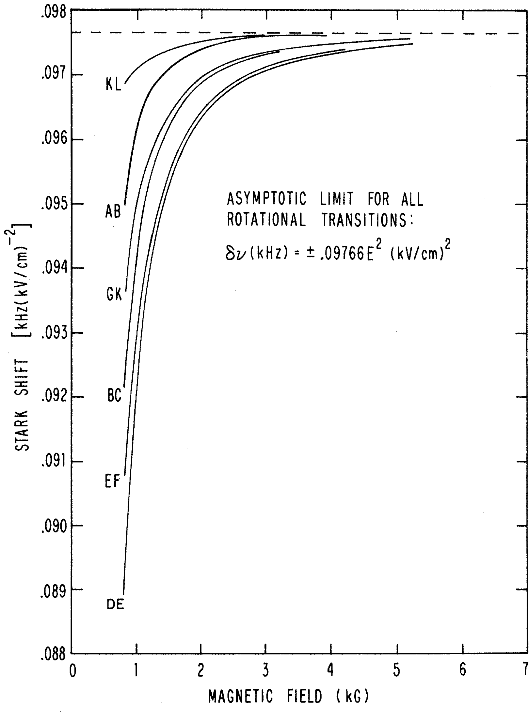

FIG. 5. Magnitude of the Stark shifts of the rotational resonances of D_2 at intermediate magnetic fields. The asymptote corresponds to the theoretical anisotropy from Ref. 4.

6.9×10^{-4}. The theoretical efficiency could apparently be obtained by redesign of the ion optics and mass spectrometer. An uncertainty of about ±40% must be allowed for the detector calibration, including uncertainties in the neutral beam intensity, the dimensions of the active region of ionization, and the mean kinetic energy of the ionizing electrons. The efficiency for beam detection varies as σ/β and can therefore be predicted for other molecules and temperatures. For an argon beam at room temperature, the over-all efficiency for detection should be 8.4×10^{-3} or $\frac{1}{119}$. Before mass selection the efficiency should be 6.2% in this case.

The ratio of detected D_2^+ ions to background ions in these experiments was 10 : 1 so that the background noise was insignificant. The H_2 beam-to-background ratio was only 1 : 50 because of the much larger background of H_2^+ ions in the detector even at an ion gauge pressure of 4.5×10^{-9} torr. However, it was still possible to obtain satisfactory data because of the low over-all noise of the detector.

The uniform static magnetic field in the C region of the apparatus was provided by an electromagnet with laminated pole faces designed according to a principle first suggested by Purcell[41] to improve the field uniformity. A precision-machined layer of Hipernom[42] 4.8 mm thick was affixed to each iron pole piece of the magnet, separated by a precision-machined layer of brass 1.6 mm thick. The laminations were bonded together with Loctite No. 307 adhesive.[43] The very high permeability of the Hipernom ($\mu = 40\,000$ at 40 G, $\mu = 400\,000$ at 3500 G) provided at low-reluctance path for magnetic flux parallel to the pole surfaces which smoothed out the spatial nonuniformities introduced by imperfections in the magnet yoke. The magnetic field varied over a range no greater than 130 mG at 1150 G in the region traversed by the molecular beam ($48\times0.8\times0.1$ cm). Use of the laminated poles also eliminated C field nonuniformities resulting from flux leakage from the adjacent A and B deflecting magnets. During the experiments the magnetic field was stabilized by a feedback system based on a Varian Hall-effect gaussmeter model No. FH-20. The magnetic field was stable within ±10 mG during each experimental run.

The uniform static electric field was provided by a pair of parallel glass plates coated with conducting layers of chromium between which voltages up to 4000 V were applied. The electric field plate assembly, including resonance coils, was inserted between the poles of the C magnet with the electric and magnetic fields parallel to within 1°. The molecular beam passed between the plates along their length. The plates were made of Starlux glass, $36\times2\times0.15$ cm, and were ground and polished for optical flatness on one side. The flatness over distances of about 4 cm was better than $\frac{1}{2}\lambda$ at 5876 Å. The flat side of each plate was vacuum coated with a semitransparent 700-Å layer of chromium and a 1200-Å layer of SiO. The plates were separated along their edges at 2.8-cm intervals by identical quartz spacers approximately 0.154 cm thick. The thickness of the spacers was compared by interferometric methods against standards traceable to the National Bureau of Standards,[44] and the thickness measurements were accurate to within 2.5×10^{-6} cm. It was possible to check the parallelism and uniform spacing of the plates after assembly by observing Haidinger's fringes[45] in diffuse monochromatic light. The plate spacing varied only $\pm44\times10^{-6}$ cm over the region traversed by the molecular beam. The relative uncertainty in spacing was taken to be $\pm3\times10^{-4}$. The potential difference between the plates was supplied by a Fluke model No. 410B high-voltage power supply. The voltages were measured by a Keithley 100 : 1 precision voltage divider model No. 6601A and a Fluke digital voltmeter model No. 8300A (DVM). The accuracy of the voltage divider and DVM was verified to within ±0.01% up to 1200 V by comparison with the direct readings of a Hewlett-Packard digital voltmeter model No. 3460B. The relative uncertainty in measurements of voltage was taken to be $\pm2.5\times10^{-4}$.

The fact that the parallelism of the electric and magnetic fields could not be guaranteed within much less than 1° requires us to make a relative correction of -1.2×10^{-4} in the assumed values of E. This follows from the fact that the Stark shifts are reduced for small angles θ_E by a factor $\frac{1}{2}(3\cos^2\theta_E - 1)$ and thus that a deviation of either sign from $\theta_E = 0$ would reduce the Stark shift for a given electric field.

Resonance coils were positioned around each end of the plates to give an oscillating magnetic field perpendicular to the static fields. The two coils were separated by 15.4 cm, and the method of separated oscillatory fields was used.[3] The phase of rf (250–1500 kHz) in the second coil was reversed at 17 Hz, and lock-in detection was used to extract the resonances from the detected background and the nonresonating beam.

The spectrum of rotational resonances of D_2 was measured at electric fields from 0 to $E = 2.5\times10^4$ V/cm at $H = 1176$ G. A typical resonance linewidth was 550 Hz. As a demonstration of the signal-to-noise ratio and the degree of symmetry of the line, a chart record of one of the stronger rotational resonances in D_2 is shown in Fig. 6. Line centers were ordinarily determined by measuring the frequencies of the half-intensity points of the central maximum. The complete six-line spectrum was

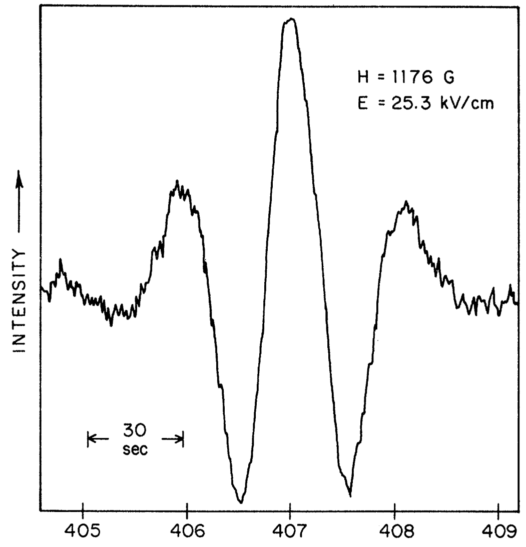

FIG. 6. Resonance *EF* in the $J=1$ state of D_2 in parallel electric and magnetic fields. The time constant of the lock-in amplifier was 1 sec.

measured in runs 2 and 4 and the stronger resonances *EF* and *GK* only were measured in runs 3 and 5. Line centers of *EF* and *GK* were reproducible during a run to ±3 Hz, whereas *AB*, *BC*, *DE*, and *KL* were reproducible to ±8 Hz. In all, 55 Stark-shifted resonances were measured of which 28 were *EF* and 19 were *GK*. *EF* was observed also at 2150 G for three electric fields in Run 1. In H_2 only *EF* was suitable for study because of the much larger beam deflections as well as the smaller beam-to-background ratio. Seven Stark shifts of *EF* were measured in H_2 at 1176 G in run 6. The linewidth was 850 Hz, and the line centers could be located to ±10 Hz. The approximate magnetic field was determined from the frequency of the strong deuteron resonance in the $J=0$ state of D_2. But for the analysis of the Stark-shift data the assumed magnetic field was that which exactly predicted the observed rotational resonance frequencies at $E=0$. This method compensated for slight inaccuracies in the assumed hyperfine constants without introducing a significant error in the measured values of γ.

IV. RESULTS

Least-squares values of γ were found separately from the six rotational resonances *AB*, *BC*, *DE*, *EF*, *GK*, and *KL* in D_2 and from *EF* in H_2. The values from a particular resonance were reproducible at 1176 G on different days within 0.01%. The mean values are listed in Table I. The only significant deviation of the Stark shifts from their calculated E dependence was at low electric fields (7–10 kV/cm) for which the frequencies of *EF* and *GK* (runs 2, 3, 5, and 6) were greater by as much as 30 Hz than those calculated from the optimum values of γ. The standard deviations of the remaining measured frequencies ($E = 15$–25 kV/cm) with respect to the calculated frequencies were 8 Hz or less. Since *EF* shifts toward lower frequencies and *GK* toward higher frequencies, the deviations at low E cannot be explained by a large hyperpolarizability or a nonlinear relationship of voltage and electric field. Likewise, line pulling,[46] the Bloch-Siegert effect,[3] and motional fields have been found incapable of producing these deviations, although an instrumental effect has not been ruled out altogether. However, the values of γ deduced from the data were influenced by less than one part in 10^4 by the data at low electric fields because the Stark shifts at large E have a much stronger effect on the deduced γ. All the observed shifts were included in reaching the results in Table I. The purely statistical uncertainty of the values in the table is about ±0.01%.

Table I shows that $\gamma(D_2)$ for *EF* at 2150 G lies above that at 1176 G by 0.1%. No explanation for this fact has been found and it would be desirable to measure γ at several magnetic fields in the future. Although the final results quoted here will be consistent with run 1, these three measurements will be ignored in the following discussion.

Table I also shows that $\gamma(D_2)$ varies among the rotational resonances at 1176 G over a range of almost 0.1% or ten times the statistical uncertainties. The Bloch-Siegert effect, the nonparallelism of $\vec{E}$ and $\vec{H}$, motional fields, and rf-power-dependent shifts are all incapable of explaining the variation of γ. The mean $\gamma(D_2)$ is calculated by weighting according to the number of data, and the result is

$$\gamma(D_2)/h = 0.48975(60) \times 10^{-3}\ \text{Hz}\ (\text{V/cm})^{-2}\ ,$$

where the uncertainty in the last digit is indicated by the number enclosed in parentheses, which is three times the rms deviations of the γ's in Table I from this mean. When the uncertainties in the

TABLE I. Mean Values of γ/h.

Molecule	H(G)	Resonance	Runs[a]	No. shifts	Mean γ/h [10^{-3} Hz(V/cm)$^{-2}$]
D_2	2150	*EF*	1	3	0.490 04
D_2	1176	*AB*	2,4	2	0.489 95
D_2	1176	*BC*	2,4	2	0.489 75
D_2	1176	*DE*	2,4	2	0.489 87
D_2	1176	*EF*	2,3,4,5	28	0.489 57
D_2	1176	*GK*	2,4,5	19	0.490 00
D_2	1176	*KL*	2,4	2	0.489 67
D_2	1176	Weighted mean		55	0.489 75
H_2	1176	*EF*	6	7	0.506 36

[a] Run numbers: 1, April 19; 2, April 22; 3, April 23; 4, April 24; 5, April 25; 6, April 26, 1971.

spacing of the electric field plates, in the voltages, and in the angle between the supposedly parallel electric and magnetic fields are combined, the total uncertainty in $\gamma(D_2)$ is ±0.15%. Therefore we have

$$\gamma(D_2) = 0.2917(4)\ \text{Å}^3\ .$$

Since it is not known whether the same discrepancies would be observed in H_2, the results here are quoted with an uncertainty ±0.18% sufficient to cover the same effects:

$$\gamma(H_2) = 0.3016(5)\ \text{Å}^3\ .$$

The ratio $\gamma(H_2)/\gamma(D_2)$ is determined to a relative accuracy ±0.23% because any errors in the plate spacing or field parallelism cancel. Therefore we have

$$\gamma(H_2)/\gamma(D_2) = 1.034(2)\ .$$

The apparent 0.1% variation of $\gamma(D_2)$ among the rotational resonances at 1176 G suggests that the observed effects might be attributed instead to possible alterations with electric field of the rotational magnetic moment μ_J, the quadrupole interaction eqQ, and the spin-rotation constant c, all of which depend upon the electronic wave functions of the molecule. On this assumption, the greatest part of the apparent variation of γ would correspond to a relative increase in μ_J of $(7 \pm 1) \times 10^{-14} E^2$, where E is in V/cm. This implies a relative decrease in the electronic contribution to μ_J by about $(1.3 \times 10^{-13})E^2$. An apparent increase in eqQ of $(2.4 \pm 1) \times 10^{-13} E^2$ could contribute a small part of the variation, and the change of c would be statistically insignificant. Two separate calculations were done to estimate theoretically the change of the rotational magnetic moment in an electric field. The first calculation used estimates of the first-order-corrected electronic wave functions in Wick's sum-over-states formula for the electronic contribution to μ_J.[47] The second was a crude classical calculation in which the ground-state electronic wave function at $E = 0$ was replaced by effective point charges at the nuclei. Both calculations implied that the relative *increase* in the electronic contribution to μ_J is approximately $(\alpha E/ea_0)^2$ when $\vec{E}$ lies along the internuclear axis and that perpendicular fields produce no change in μ_J to this order. The estimates differ in sign from the observed effect and are five orders of magnitude smaller. Therefore it is unlikely that the E dependence of μ_J is really the cause of the variations in Table I. A careful study of the instrumental effects known to occur in experiments of this type has failed to reveal the answer, but instrumental effects cannot be ruled out altogether. More extensive data at the present level of precision would be helpful.

TABLE II. Experimental values of $6c + 9d$ in D_2 from Eq. (14).

E (V/cm)	Run	$6c + 9d$ (Hz)
0	2	279 741(26)
0	4	279 723(26)
2.4×10^4	2	279 788(26)
2.4×10^4	4	279 763(26)
...	...	279 781(22)[a]

[a] Reference 38.

TABLE III. The dependence of D_2 nuclear magnetic shielding on orientation.

E (V/cm)	Run	$2(\sigma_{\pm 1} - \sigma_0)a$ (Hz)
0	2	-11.1 ± 14
0	4	-22.2 ± 14
2.4×10^4	2	-13.5 ± 14
2.4 ± 10^4	4	-20.3 ± 14
Mean value	...	-16.8 ± 14 Hz
$\sigma_{\pm 1} - \sigma_0 = -11 \pm 9$ ppm		
$\Delta\sigma = \sigma_\pi - \sigma_\sigma = 27 \pm 23$ ppm		

Because the six rotational resonances in D_2 were observed at the same magnetic field in run 2 and again in run 4, it was possible to apply two relationships among the transition frequencies as a check of the molecular hyperfine constants. Bray[48] has shown by an exact solution of the secular equation that

$$2(GK - BC) + (EF - DE) + (KL - AB) = 6c + 9d \tag{14}$$

and

$$(EF + DE) - (KL + AB) = 2(\sigma_{\pm 1} - \sigma_0)a\ . \tag{15}$$

Here d is the constant describing the combined effects of the nuclear spin-spin interaction and the quadrupole interaction, $a = \mu_D H/h$ where μ_D is the deuteron magnetic moment, and $(\sigma_{\pm 1} - \sigma_0)$ is the difference in the nuclear magnetic shielding of D_2 in the $m_J = \pm 1$ and $m_J = 0$ states.[32] Equations (14) and (15) are valid in the presence of an electric field since the electric polarizability (when $\vec{E} \parallel \vec{H}$) enters the Hamiltonian in the same form as the magnetic susceptibility, which was included in the exact solution. The corrections for line pulling were applied to the resonance frequencies in runs 2 and 4, and the left-hand side of Eq. (14) was calculated. The results are shown in Table II. The quantities obtained at $E = 2.4 \times 10^4$ V/cm were higher than those at $E = 0$, reflecting possible small apparent increases in c and eqQ discussed above. The current best experimental value of $6c + 9d$ for D_2 in the $J = 1$ state is listed for comparison.[38]

TABLE IV. Experimental and theoretical values of the anisotropy of the static polarizability of H_2 and D_2.

Quantity	Conditions	Experimental (Å^3)	Theoretical[a] (Å^3)
$\gamma(H_2)$	$J=0$	0.304(5)[b]	0.2999
	$J=1$	0.276(8)[c]	0.3011
	$J=1$	0.3016(5)[d]	0.3011
	normal, 293 K	0.305[e]	0.3017
	normal, 293 K	0.299[b]	0.3017
$\gamma(D_2)$	$J=0$	0.289[b]	0.2902
	$J=1$	0.290(+3, −9)[f]	0.2908
	$J=1$	0.2917(4)[d]	0.2908
$\gamma(H_2)/\gamma(D_2)$	$J=1$	1.034(2)[d]	1.0354

[a] Kołos and Wolniewicz (Ref. 4).
[b] Bridge and Buckingham, see text (Ref. 28).
[c] Nelissen, Reuss, and Dymanus, see text (Ref. 30).
[d] Present work.
[e] Rowell, Aval, and Barrett, see text (Ref. 29).
[f] English and MacAdam (Ref. 1).

Table II shows a slight difference between the present measurements at $E=0$ and those of Code and Ramsey, but the difference is barely greater than the combined uncertainties.

Equation (15) can be used to find the dependence of nuclear magnetic shielding in D_2 on molecular orientation,[2,32] which has not previously been reported. The results are shown in Table III. Cook *et al.*[49] predict for H_2 a value $\Delta\sigma = 2.2$ ppm, and the value for D_2 should be approximately the same. Although the experimental result for $\Delta\sigma$ is about 12 times larger than the theroretically predicted value, the measured value is only slightly greater than its uncertainty, and so little significance can be attached to the value. Measurements at higher magnetic fields with the present apparatus could reduce the uncertainty by at least 50%.

V. DISCUSSION

The results of the present experiments are given in Table IV with the experimental results of other authors and the corresponding theoretical predictions of Kołos and Wolniewicz (KW). The values of $\kappa = \gamma/3\alpha$ derived from measurements of Rayleigh depolarization ratios at $\lambda = 6328$ Å by Bridge and Buckingham[28] and at $\lambda = 4880$ Å by Rowell *et al.*[29] have been extrapolated to $\lambda = \infty$ by scaling the polarizability according to the results of Victor and Dalgarno.[50] Bridge and Buckingham presented κ in a form comparable with the polarizabilities of the $J=0$ states of H_2 and D_2. Therefore the average polarizabilities α in the $J=0$ states calculated by KW have been used to infer experimental values of the static anisotropy, and these are listed opposite the anisotropies calculated by KW in the $J=0$ states. Rowell *et al.* list two independent measurements of the depolarization ratio for H_2 in a form comparable with the polarizabilities for a rotational ensemble at room temperature. Therefore α calculated by KW as a rotational average at 293 K has been used to infer experimental values of γ and these are listed opposite the rotationally averaged γ calculated by KW. The static anisotropy attributed to Nelissen *et al.*[30] is derived from their independent measurements of α and κ in the $J=1$ state of H_2. The uncertainties given by the authors have been combined in quadrature.

Table IV shows that in the present work the uncertainty in measurements of γ has been reduced by an order of magnitude compared with previous experiments. Our result for H_2 differs from the calculations of KW by +0.17% and the uncertainty is ±0.18%. Our result for D_2 differs from KW by +0.3% whereas the uncertainty is only ±0.15%. Our measured value of the ratio $\gamma(H_2)/\gamma(D_2)$ falls below the calculation by 0.14% and the uncertainty is 0.2%. Therefore the calculated values of the anisotropy of the static polarizability of H_2 and D_2 have been verified experimentally within a fraction of a percent although there is some evidence that the value calculated for D_2 is slightly low. It should be possible to reduce the experimental uncertainties even more in further experiments of the type reported here.

ACKNOWLEDGMENTS

We are grateful to Dr. T. C. English for suggesting this experiment and for several helpful discussions in the course of the work. J. Vitkevich constructed the new C magnet poles and helped in the analysis of the data. The physics department's AEC-supported computer provided free computing time.

[†] Work supported in part by the National Science Foundation.

[*] Present address: Physics Department, University of Stirling, Stirling, Scotland.

[1] T. C. English and K. B. MacAdam, Phys. Rev. Letters 24, 555 (1970).

[2] N. J. Harrick, R. G. Barnes, P. J. Bray, and N. F. Ramsey, Phys. Rev. 90, 260 (1953).

[3] N. F. Ramsey, *Molecular Beams* (Oxford U. P., New York, 1956), pp. 162 and 124.

[4] W. Kołos and L. Wolniewicz, J. Chem. Phys. 46, 1426 (1967).

[5] R. L. Wilkins and H. S. Taylor, J. Chem. Phys. 48, 4934 (1968).

[6] D. F. T. Tuan, Chem. Phys. Letters 7, 115 (1970).

[7] J. M. Schulman and D. N. Kaufman, J. Chem. Phys. 53, 477 (1970).

[8] A. Saika, J. I. Musher, and T. Ando, J. Chem. Phys. 53, 4137 (1970).

[9] A. J. Sadlej, Theoret. Chim. Acta 21, 159 (1971).

[10] T. K. Lim and B. Linder, Theoret. Chim. Acta 19, 38 (1970).

[11] P. W. Langhoff and M. Karplus, J. Chem. Phys. 52, 1435 (1970).

[12] H. P. Kelly, Phys. Rev. Letters 23, 455 (1969); Phys. Rev. A 1, 274 (1970).

[13] N. S. Hush and M. L. Williams, Chem. Phys. Letters 6, 163 (1970).

[14] I. R. Epstein and W. N. Lipscomb, Chem. Phys. Letters 4, 479 (1970).

[15] D. W. Davies, Mol. Phys. 17, 473 (1969).

[16] M. Cohen and B. W. Southern, Can. J. Phys. 48, 1991 (1970).

[17] T. C. Caves and M. Karplus, J. Chem. Phys. 50, 3649 (1969).

[18] T. Ando and A. Saika, J. Chem. Phys. 55, 4203 (1971).

[19] A. Dalgarno, A. L. Ford, and J. C. Browne, Phys. Rev. Letters 27, 1033 (1971).

[20] D. M. Golden and B. Crawford, Jr., J. Chem. Phys. 36, 1654 (1962).

[21] Kan Kuei-Chaio, Chinese J. Phys. (Taipei) 8, 58 (1970).

[22] R. W. Terhune and C. W. Peters, J. Mol. Spectry. 3, 138 (1959).

[23] H. L. Buijs and H. P. Gush, Can. J. Phys. 49, 2366 (1971).

[24] J. P. Colpa-Boonstra and J. A. A. Ketelaar, Mol. Phys. 1, 343 (1958).

[25] H. Moerkerken, M. Prior, and J. Reuss, Physica 50, 499 (1970); H. Moerkerken and J. Reuss, in *Electronic and Atomic Collisions: Abstracts of the Seventh International Conference on the Physics of Electronic and Atomic Collisions* (North-Holland, Amsterdam, 1971), p. 663.

[26] H. L. Kramer and D. R. Herschbach, J. Chem. Phys. 53, 2792 (1970).

[27] G. A. Victor and A. Dalgarno, J. Chem. Phys. 53, 1316 (1970).

[28] N. J. Bridge and A. D. Buckingham, Proc. Roy. Soc. (London) A295, 334 (1966).

[29] R. L. Rowell, G. M. Aval, and J. J. Barrett, J. Chem. Phys. 54, 1960 (1971).

[30] L. Nelissen, J. Reuss, and A. Dymanus, Physica 42, 619 (1969).

[31] A similar technique has been used to measure the anistropy of the electric polarizability of various atoms by N. J. Martin, P. G. H. Sandars, and G. K. Woodgate, Proc. Roy. Soc. (London) A305, 139 (1968); A. T. Ramsey and R. Petrasso, Phys. Rev. Letters 23, 1478 (1969); and M. A. Player and P. G. H. Sandars, Phys. Letters 30A, 475 (1969).

[32] N. F. Ramsey, Phys. Rev. 85, 60 (1952).

[33] A. R. Edmonds, *Angular Momentum in Quantum Mechanics*, 2nd ed. (Princeton U. P., Princeton, New Jersey, 1960), pp. 25 and 63.

[34] All tensor elements not obtained from these by permutation of indices are zero because of symmetry.

[35] A. D. Buckingham and B. J. Orr, Proc. Roy. Soc. (London) A305, 259 (1968).

[36] M. R. Baker, H. M. Nelson, J. A. Leavitt, and N. F. Ramsey, Phys. Rev. 121, 807 (1961).

[37] I. Ozier, Ph.D. thesis (Harvard University, 1965) (unpublished).

[38] R. F. Code and N. F. Ramsey, Rev. Sci. Instr. 42, 896 (1971).

[39] R. Weiss, Rev. Sci. Instr. 32, 397 (1961).

[40] L. J. Kieffer and G. H. Dunn, Rev. Mod. Phys. 38, 1 (1966).

[41] L. S. Goodman, Rev. Sci. Instr. 31, 1351 (1960).

[42] Manufactured by Westinghouse Electric Corp., Materials Manufacturing Division, Blairsville, Pa. (Hipernom alloy).

[43] Manufactured by Loctite Corp., Newington, Conn. (No. 307 adhesive).

[44] Van Keuren Co., Watertown, Mass.

[45] J. Strong, H. V. Neher, A. E. Whitford, C. H. Cartwright, and R. Hayward, *Procedures in Experimental Physics* (Prentice-Hall, New York, 1938), p. 66.

[46] N. F. Ramsey, in *Recent Research in Molecular Beams*, edited by I. Estermann (Academic, New York, 1959), p. 107.

[47] G. C. Wick, Phys. Rev. 73, 51 (1948).

[48] P. J. Bray, Ph.D. thesis (Harvard University, 1952) (unpublished).

[49] D. B. Cook, A. M. Davies, and W. T. Raynes, Mol. Phys. 21, 113 (1971); W. T. Raynes, A. M. Davies, and D. B. Cook, *ibid.* 21, 123 (1971).

[50] G. A. Victor and A. Dalgarno, J. Chem. Phys. 50, 2535 (1969).