ONE-ELECTRON PROPERTIES OF THE WATER MOLECULE

by

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PROEFSCHRIFT

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CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

Water is one of the most important molecules in chemistry and biology. Explanation of its properties in terms of molecular charge and current distributions have long been a challenging goal of experimental and theoretical investigations. As one of the simplest nonlinear polyatomic molecules and with several isotopic species ($\text{H}_2\text{O}$, $\text{HDO}$, $\text{D}_2\text{O}$, $\text{H}^{18}\text{O}$) readily accessible to careful measurements, water is a proving ground for ab-initio calculations in molecular quantum mechanics. From a theoretical point of view it is a prototype of tristatic molecule since only one of the three atoms involved has closed inner shells.

The classic paper of Ellison and Shall (Ell 55) and a few others which followed it (See 60, Bis 66, Han 67, Mag 67), dealt primarily with gross bonding properties and yielded in addition the geometrical parameters, the total and one-electron energies, and in some cases the values of the electric dipole moment and of the vibrational frequencies. The results were encouraging or discouraging depending on the way one looked at them.

It has been pointed out that a satisfactory total energy does not necessarily imply a good description of the charge distribution (Mol 62). In consequence, one has to include also one-electron properties in testing the performance of the molecular wave function.

Recently several SCF calculations on the ground state of the water molecule became available, which include also the expectation values of one-electron properties which depend only on the electronic ground state. Harrison (Har 67) used Gaussian lobe functions as a basis set for his calculations, while Aung et al. (Aun 68) used Slater type orbitals, and Neumann and Monkovits (Neu 68) the contracted and uncontracted Gaussian functions. These authors calculated the molecular electric dipole moment, the molecular electric quadrupole moment, the gradient of the electric field at the deuteron and the oxygen nucleus, the
diamagnetic shielding of the proton and the oxygen nucleus, and the diamagnetic susceptibility of the water molecule.

At the start of this work only the experimental values of the dipole moment and of the components of the gradient tensor at the proton as well as at the oxygen nucleus were known. The absolute value for the dipole moment was determined from Stark effect of the rotational transitions of water (Bel 67). The quadrupole coupling tensor of $^{17}$O was determined by Stevenson and Townes (Ste 57) from the hyperfine structure of the $^{2}_2 -^{2}_1$ rotational transition of $^{17}$D$_2$O using a conventional microwave spectrometer. The low resolution of their spectrometer casts heavy doubt upon reliability of the results. Accurate values for the electric field gradient tensor at the proton nucleus were determined by Bluyssen et al. (Blu 67) from the hyperfine structure of a number of rotational levels of D$_2$O and HD by beam-maser spectroscopy.

It was first shown by Harrick and Ramsey (Har 52), by Townes et al. (Tow 56a), and later on by Gräff and coworkers (Dre 61, Grä 63, Grä 65, Grä 65a) that some of the remaining one-electron properties: the molecular quadrupole moment, the sign of the electric dipole moment, and the anisotropies in the diamagnetic shielding and in the diamagnetic susceptibility can be determined from accurate measurements of the Zeeman effect of rotational levels of the isotopic species of a molecule. However, at the start of this work no accurate measurements of the Zeeman effect of water were available to determine these quantities.

The present investigation was intended primarily to determine experimentally the hitherto unknown or only poorly known one-electron properties of the water molecule. To this end the hyperfine interactions and the Zeeman effect of rotational levels of isotopic species of water are accurately investigated with a beam-maser Zeeman spectrometer.

The high sensitivity, necessary for these experiments, is obtained by the application of beam modulation and phase sensitive detection in combination with time averaging techniques. The results may be used to investigate to what extent the hyperfine interactions, due to the proton and to the deuteron, depend on the rotational state and on isotopic substitution.

The first group of experiments comprises zero field measurements on the $^{2}_1 -^{2}_0$ transition of HD, the $^{2}_1 -^{2}_0$ transition of HD$^{17}$O, the $^{2}_1 -^{2}_1$ transition of D$_2$O, and on the $^{2}_1 -^{2}_1$ transition of H$_2$O. These measurements supplement the available (Blu 67, Blu 68) experimental data on hyperfine interactions of rotational levels of isotopic species of water and also serve as a check on the coupling tensors are really molecular constants. The results on the $^{2}_1 -^{2}_1$ transition of HD$^{17}$O are used to determine the electric field gradient at the oxygen nucleus.

The second group of experiments deals with accurate determination of the Zeeman effect of rotational transitions of isotopic species of water. From the splitting pattern of these transitions accurate values of the molecular magnetic moment, of the magnetic susceptibility, and of the magnetic shielding are obtained.

Four rotational transitions are selected for the measurements because of their high signal to noise ratio. The two transitions of D$_2$O enable us to determine the elements of the molecular magnetic tensor, the magnetic susceptibility tensor, and the magnetic shielding tensor. The elements of the molecular quadrupole tensor can then be calculated from the experimental data on magnetic moments and magnetic susceptibilities. The Zeeman effect of a transition of HD and of H$_2$O is measured to include isotopic effects and to determine the sign of the electric dipole moment.

With these experimental results it is hoped to investigate the performance of the several basis sets used in the evaluation of the molecular charge distribution.

1.2 HYPERFINE STRUCTURE OF ROTATIONAL SPECTRA

Hyperfine structure in the microwave spectra of $^{1}$H molecules originates in the interactions of the nuclear moments with the internal fields. In the rough order of descending magnitude of the interaction energy these interactions in the case of asymmetric molecules are:

1. the nuclear electric quadrupole interaction,
2. the nuclear spin-rotation interaction, and
3. the direct nuclear spin-spin interaction.

The first interaction arises from the coupling of the nuclear
electric quadrupole moment with the gradient of the electric field at a given nucleus. The contributions to the gradient come from other nuclei and from the molecular electrons. The nuclear part can be calculated from the known molecular geometry. The electronic part depends only on the wave function of the molecular ground state. The quadrupole interaction of $^{13}$C gives rise to a hyperfine splitting typically from about 100 kHz up to about 2 MHz. The quadrupole moment of the deuteron yields splittings of about 50 kHz.

The nuclear spin rotation interaction in a molecule, having a $^1S$ electronic ground state, arises from the interaction of a nuclear magnetic dipole moment with the effective magnetic field at the nucleus. The effective field depends on the rotation of the bare nuclear frame and on the excitation of electrons into higher electronic states with non-zero angular momentum by the molecular rotation. The contribution of the spin-rotation interaction to the hyperfine energy is generally smaller than the contribution of the deuteron quadrupole coupling.

The direct nuclear spin-spin interaction is the well known interaction between two magnetic dipoles. The magnitude of the interaction energy can be calculated from the molecular geometry and the known values of the nuclear magnetic moments. It is generally smaller than the spin-rotation interaction.

A review of the literature and of the experimental and theoretical results on these interactions are given elsewhere (Tom 55, Hui 66, Lee 66, Wac 67, Hui 68).

1.3 ZEEMAN EFFECT IN ROTATIONAL SPECTRA

A freely rotating $^1S$ molecule (zero orbital and zero spin electronic angular momentum) interacts with an external magnetic field by two mechanisms.

The first mechanism is the interaction of nuclear magnetic moments and of the magnetic moment induced by the molecular rotation with the external magnetic field $\vec{B}$. The energy of these interactions can be written as $-\mu \cdot \vec{B}$, where $\mu$ is one of the magnetic moments. This is clearly the linear Zeeman effect.

The second mechanism involves perturbation of the molecular charge distribution by the external magnetic field. The reaction of the molecular electrons to the applied field results in an induced molecular magnetic moment proportional to the field, the constant of proportionality being the magnetic susceptibility. Consequently the interaction energy of the induced molecular magnetic moment with the applied magnetic field depends on $\mu^2$. In addition, the reaction of the electrons leads to a shielding of the nuclear magnetic moments from the applied field. This effect is known as "chemical shift" in nuclear magnetic resonance spectroscopy.

The induced molecular magnetic moment depends generally on the direction of the magnetic field in the system of reference fixed in the molecule. This dependence is usually represented by a cartesian tensor of the second rank. The hyperfine and the remaining magnetic interactions involve also similar tensors.

The molecular magnetic moment tensor, the magnetic susceptibility tensor, and the magnetic shielding tensor are rather complicated functions of the electronic states as discussed in Chap. 3.

The molecular magnetic moment tensor consists of a nuclear and an electronic part. The electronic part is paramagnetic and depends both on the ground and on excited electronic states. Magnetic susceptibility and magnetic shielding tensors both consist of a paramagnetic and a diamagnetic part. The diamagnetic part depends only on the electronic ground state.

As will be shown in Sect. 5.4, the paramagnetic part of the magnetic susceptibility is proportional to the paramagnetic contribution to the molecular magnetic moment. The proportionality constant depends only on the molecular geometry. A similar parallelism occurs between the paramagnetic part of the magnetic shielding and of the electronic part of the spin-rotation interaction of the same nucleus. Using these relations, average values over the electronic ground state of various operators as well as some information on excited electronic states can be obtained from the measured interaction constants.

Burke and Strandberg (Bur 53) measured previously the molecular magnetic moments of water and obtained values of about 0.5 kHz$^{-1}$, using conventional microwave spectrometers whose resolution was about 500 kHz. The resolving power of the present spectrometer is increased.
by a factor of 100 over that of Burke and Strandberg. This enables us to measure the g-values more precisely.

At the start of this investigation no measurement of magnetic susceptibility and shielding effects on rotational levels of asymmetric top molecules were known. The corresponding energy splittings are of the order of 1 KHz at 10 kHz. The application of magnetic fields strengths of up to 12 kG in the present spectrometer yields measurable energy splittings because of these effects.

In papers which appeared while this work was in progress, Hüttner et al (Klt 68), Hüttner and Flygare (Klt 69), and Sutter et al (But 69) reported the measurements of magnetic susceptibility effects in the microwave spectrum of formaldehyde, fluoroacetic acid, and ethylene oxide.

1.1 THE BEAM-MASER ZEEMAN SPECTROMETER

At fields of about 20 kG, readily obtainable with ordinary laboratory magnets, the magnetic susceptibility and shielding effects of water yield energy splittings of up to a few KHz. It is therefore very difficult to resolve these effects by conventional microwave spectroscopy. The ultimate resolution of a high resolution spectrometer is determined by Doppler broadening and by the Uncertainty Principle. The use of molecular beams to reduce Doppler broadening was well recognized long ago. However, all spectrometers in the microwave region using this technique suffered of low sensitivity and found little application. Gordon et al (Mor 51a) showed that this limitation can be removed in some cases by the application of the maser principle. Practical realization of this principle is the beam-maser spectrometer which combines high resolution with good sensitivity. Other successful high resolution spectrometers are: the molecular beam magnetic and electric resonance spectrometers, and the molecular beam millimeter-wave spectrometer. The ultimate resolution of all these spectrometers is usually determined by the Uncertainty Principle. More detailed information about these and several other high resolution spectrometers is given by several authors (Tha 61, Fiy 64, Hul 66, Wac 67, Blu 68).

Previous measurements on the hyperfine structure of H₂O, HDO, and D₂O (Fos 60, Tre 62, Tha 64, Hul 66, Blu 67,68a) showed that the best high resolution spectrometer, as far as resolving power and signal to noise ratio of rotational transitions of water are concerned, is the beam-maser spectrometer. The operation of the spectrometer is based upon the phenomenon of stimulated emission of molecules in a molecular beam. A simplified diagram of a beam-maser spectrometer is shown in Fig.2.1.

The molecules emerging from the channels of a Zacharias oven pass through an electrostatic state selector before interaction occurs with electromagnetic radiation in a microwave cavity. The octopole state selector exerts a force on a molecule in the beam. This force depends on the Stark energy of the specific molecular state. Molecules in certain quantum states will be removed from the beam while molecules in other states are more likely to enter the microwave cavity.

In the absence of any state selection, only the small difference in population between the lower and the upper energy level involved in the transition contributes effectively to the absorption. When state selection is applied all molecules of the lower state can in principle be removed from the beam. The molecules entering the cavity are then all in the upper state from which they are stimulated to emit coherently by the electromagnetic field of the cavity. As the number of molecules in the upper state is much larger than the population difference of the upper and lower state, the emitted power is also much larger than the absorbed power. This results in a gain in sensitivity which may be many orders of magnitude.

In a beam-maser Zeeman spectrometer the cavity is placed in an external magnetic field in order to observe Zeeman effect of the rotational levels. The homogeneity and stability of the field in the cavity must fulfill several requirements to prevent line broadening of Zeeman transitions.

It is clear from the foregoing that Stark effect plays a dominant role in the application of beam-maser Zeeman spectroscopy. The rather stringent requirements for the Stark effect are generally fulfilled when there are two isolated energy levels between which an electric dipole transition is allowed.

In addition to the inversion transitions of ammonia (NH₃), the slightly asymmetric light polar molecules (HDO, D₂O, H₂O, HDS, HD₆E, 

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CHDo) have often such pairs of rotational levels separated by a microwave frequency. Transitions of molecules with hindered rotation, such as CH3OH and H2O2 (Ver 66, Mee 69), and transitions between the components of a A-doublet of OH (Mee 69) may also have a favorable Stark effect. Although they do not have well isolated pairs of energy levels, some transitions of strongly polar linear molecules as C12H, ICIH, BrCN (Tha 60) may also be investigated by a beam-maser Zeeman spectrometer. While this work was in progress, Shigenari (Shi 67) reported the construction of a beam-maser Zeeman spectrometer in order to investigate both the hyperfine and first order Zeeman effect of several transitions of formamide. He used magnetic fields up to 10 G with an inhomogeneity of less than one per cent.

CHAPTER 2
THE BEAM-MASER ZEEMAN SPECTROMETER

2.1 INTRODUCTION

The present beam-maser spectrometer described in Sect.2.2 is a modified version of the designs of Thaddeus et al (Tha 61) and of Blyussan (Bly 68). A substantial feature is the introduction of a stable and homogeneous magnetic field in the cavity in order to observe Zeeman effect of rotational spectra.

Most of the investigated spectra are obtained by using a superheterodyne detection scheme with phase sensitive demodulation. The required modulation of the signal power is achieved by mechanical chopping of the beam. In order to increase the signal to noise ratio, we applied in addition sample averaging techniques. To this end we developed a method to feed automatically any desired number of spectra to a computer of average transients. A general survey of the detection system is given in Sect.2.3. Sensitivity of the spectrometer, its resolving power and stability are discussed in the last section. A short discussion of the results with a few examples of the recorded spectra serves as an illustration of performance and potentialities of the spectrometer.

2.2 DESCRIPTION OF THE SPECTROMETER

2.2.1 The vacuum system

The vacuum system of the spectrometer (Fig. 2.1) consists of the main chamber housing the source, the selector chamber in which the state selector is mounted, and of a flat box containing the maser cavity. All chambers are made of stainless steel. All flanges are sealed with viton O-rings.

The main chamber, a cylinder 30 cm in diameter and 65 cm long with four cross-wise located flanges, is pumped by an oil diffusion pump with a pumping speed of 500 l/s (Levbold, DO 500).
The selector chamber, also a cylinder, with a diameter of 13 cm and a length of 35 cm, is attached to the flange pointing in the direction of the magnet. The diameter of this chamber is determined by the available space between the coils of the magnet. The chamber contains in addition to the state-selector a liquid nitrogen trap.

The last chamber of the vacuum system is a flat box (width 4.8 cm) which fits in the gap between the poles of the magnet. This box contains the microwave cavity and two liquid nitrogen traps. The cavity can be adjusted from the outside of the vacuum system by means of four screws mounted on the top side of the box. This flange contains also the input waveguide of the cavity and the connections to the thermal tuning jacket.

The pressure is measured with two ionisation gauges (Balzers I.M.), one mounted above the diffusion pump and one behind the last liquid nitrogen trap in the flat box. During operation of the spectrometer the pressure is about $5 \times 10^{-7}$ Torr. Assuming that the pressure between the two gauges does not increase above $10^{-6}$ Torr, the mean free path of the molecules will be larger than 10 m. As the molecules have to travel a distance of about 75 cm, attenuation of the beam is negligible. This is tested experimentally by increasing the pressure to a few times $10^{-6}$ Torr. The maser signal did not show a measurable decrease.

2.2.2 The molecular beam

A rigid rack consisting of four stainless steel bars is mounted at the flange of the main chamber (Fig. 2-1). The effuser, the beam-roller, the state selector, and the surrounding liquid nitrogen trap are attached to this rack. The entire unit, shown in Fig. 2-2, can easily be moved in and out of the vacuum chambers for readjustments and repairs.

Fig. 2-1. Schematic diagram of the molecular beam maser; L = liquid nitrogen trap; CL = cylindrical liquid nitrogen trap surrounding the state selector; C = microwave cavity; W = water jacket; S = state selector; BH = beam chopper; E = effuser; P = pumping unit.

Fig. 2-2. Photograph showing the rigid rack (90 cm long) with the effuser, the beam chopper, the state selector, and the surrounding liquid nitrogen trap.
The Zacharias effuser has a length of 6 mm and a diameter of 12 mm. The number of channels is about 4000. The estimated transparency is about 50 per cent.

The beam chopper consists of a circular disk, 6 cm in diameter, with a raised border of 2 cm. The border is divided into four segments; the segments No.1 and 3 are open while the segments No.2 and 4 are closed. It is driven by an a.c. hysteresis motor (Globe Industries Inc.). The modulation frequency of the beam is 120 Hz at 60 revolutions per second of the chopper. A light beam perpendicular to the molecular beam is chopped simultaneously. The 120 Hz signal produced by a photocell behind the chopper serves as a reference signal for the lock-in amplifier.

The octupole state selector is made of stainless steel rods, 2 mm in diameter and 25 cm in length. These rods are attached to perspex rings. The distance between the electrodes is 3 mm. The measurements are performed with 30-35 kV applied to the state selector.

The reflection type maser cavity oscillates in the TM 010 mode. It is made of brass. The coupling hole is adjusted by trial and error for a reflection of 60 per cent which is close to the optimum operating conditions (Tha 61). The cavity is surrounded by a water jacket. The resonance frequency of the cavity is controlled by regulating the temperature of the water flowing through the jacket by a thermostat to within 0.02°C.

Eliasson (Eli 68) discussed extensively the molecular flow through a Zacharias effuser, the action of the state selector, and the influence of the cavity on the line form. Using Eliasson's results the estimated number of molecules entering the state selector of the present spectrometer is about $10^{16}$ mol/sec, and the number of molecules in the $P_2$ state of HD entering the cavity is about $10^{13}$ mol/sec.

2.3 THE DETECTION SCHEME

2.3.1 The superheterodyne detector

Because of the very low signal-power level ($< 10^{-6}$W) the superheterodyne detection scheme, shown schematically in Fig.2-3, is used...
for the detection of the maser emission. The output power of the signal-oscillator (80) klystron at a frequency \( f_1 \) is fed to the microwave cavity. The reflected fraction of this power is transmitted to a crystal diode (N833), where it is mixed with the output of the local-oscillator (10) klystron operating at a frequency \( f_2 = 30 \text{ MHz} \). The resulting beat signal at 30 MHz is amplified by a low noise pre-amplifier (Airborne Instruments Laboratory) with a noise figure of 1.5 dB and a bandwidth of 2.1 MHz. After demodulation of the 30 MHz signal by an 1867 crystal rectifier, the signal is fed to the lock-in amplifier tuned to the chopper frequency. A constant frequency difference of 30 MHz between the LO- and the 80-klystron at any 80 frequency is secured by feeding a fraction of the amplified 30 MHz information signal to a Schonandl type PBSO synchrotron, where it is phase-locked to a 30 MHz reference signal.

The 80-oscillator is coupled to a combined Schonandl-Rohde and Schwarz frequency generating system. In this system, both the Schonandl ND30 variable oscillator (300 Hz-31 MHz) and the Rohde and Schwarz XVC frequency synthesizer (470-1000 MHz) are driven by a 10 MHz signal from the Rohde and Schwarz XEU oscillator. The oscillator is coupled to a Varian E20 rubidium frequency standard. By varying the frequency of the ND30 oscillator any arbitrary frequency between 470 and 1000 MHz may be obtained at the output of the XVC. At the crystal M higher harmonics are then generated and mixed with the 80-klystron frequency. The resulting 30 MHz beat frequency is phase locked to a 30 MHz reference signal by means of a Schonandl PBSO synchrotron. By turning the tuning knob of the ND30 oscillator with an Halsstrup synchronous motor, the 80- and LO-frequencies are swept simultaneously. The frequency of the ND30 oscillator is measured with a frequency counter (Kestrel Packard 615221). A frequency marker unit coupled to this counter generates the frequency markers which are recorded simultaneously with the spectrum.

Most spectra are measured with a sweep rate of about 230 Hz per second and a time constant of the lock-in amplifier of 1 sec. The signal to noise ratio of the unsplit lines runs up to 2000. The signal to noise ratio of the Zeeman and hyperfine components of the \( 6_{1/2} \rightarrow 5_{1/2} \) transition of \( ^12\text{CO} \) is too low to measure it with this method. These spectra are measured using time averaging techniques.

2.3.0 The method of time averaging

It is well known that the signal to noise ratio can be made, in principle, arbitrarily large by increasing the measuring time. This gain is often realized by decreasing the scan rate of the spectrometer, which allows the use of longer integration times.

Generally, long-time fluctuations and instabilities of the detection system prevent the use of time constants longer than about 30 sec. In our spectrometer such instabilities are caused by variation of the output power of the klystrons and of the pressure in the vacuum system, and by the temperature dependence of the resonance frequency of the cavity and of the gain of the detectors and amplifiers.

Instead of using the total available time for a single measurement at low sweep rate, one can scan over a number of relatively fast sweeps over the same frequency region with a correspondingly shorter time constant. In this process the information signals are added coherently while the noise tends to average because of its random nature. This method is called time averaging.

The process of adding and averaging of spectra obtained from the successive scans is performed in our experiments by a Computer of Average Transients (Technical Measurements Corporation, type CAT 105 C). The CAT contains a magnetic core memory system in which the data are stored in binary decimal code form. The memory contains 400 addresses each capable of storing 24 binary digits representing \( 10^5 \) counts in decimal form. The total memory consists of 9600 cores. When triggered by a synchronizing signal, the CAT starts to sample the data at specific intervals, converting each sample into a digital number of counts proportional to the amplitude of the input data. The synchronizing signal is either fed externally to the trigger input or generated internally. The counts are stored in a particular address after being added to the number previously stored in this address. This adding takes 36 usec for each sample. In consequence the CAT has a dead time of 400X36 usec for each scan. At a total sweep time of 16 sec, used in the present experiments, this dead time is negligible.
If we scan a spectrum n times and feed these spectra into the CAT, the signal to noise ratio increases as the square root of the number of scans, if we assume an invariant signal embedded in a wide band noise of constant amplitude. As in most experiments the number of summed spectra is proportional to the total time of measurement \( t \), the signal to noise ratio is proportional to the \( V_0 \). Ernst (Err 65) discussed the method of time averaging when correlation effects are present in the noise. In this case the square root law may lose its validity.

The accumulated data may be displayed on the cathode ray tube of the CAT or read out in either digital or analog form. Any of these operations does not affect the contents of the memory. It is thus possible to monitor the summation of the spectra during the experiment without disturbing the process. Also turning off the CAT does not erase the information stored in the memory and so it is possible to sample the spectra over a number of days.

2.3.3 Detection with a CAT

The CAT is connected to the lock-in amplifier of the superheterodyne detection scheme described in Sect. 2.3 (See also Fig. 2-3). Below we give a few details of the operation and of the associated circuitry of the CAT.

The fundamental requirement for a successful application of the sampling technique is a constant sweep rate over exactly the same frequency region at each sweep. Evidently, the start of each frequency sweep must be well synchronized to the time base of the CAT. These requirements cannot be satisfied when sweeping the 99-frequency with a Halstrupp motor at the NBSOM because of irregularities in the rotation of the motor. For this reason, the 10 MHz reference signal of the RF30 synchronizer of the SC-kylintron, set at the required starting frequency of the NBSOM, is swept with a 10 MHz sweep unit developed in the electronic workshop of the laboratory. This sweep unit operates as follows.

The signal of a variable 10 MHz generator is mixed with a 10 MHz signal from a quartz oscillator. The resulting beat frequency is converted into a voltage which is compared with a saw-tooth voltage generated independently in the unit. By feeding the difference voltage to a capacitance diode of the 10 MHz generator, a stable and linear 10 MHz sweep unit is obtained which follows the frequency of the saw-tooth voltage. The usual period of this voltage is 19 sec. At the beginning of a 19 sec period of the sweep unit, a pulse is generated which starts the CAT to average the data for 16 sec. Then the CAT waits for a new start-pulse. After 19 sec the sweep unit returns to the start frequency and starts the CAT once more, and so on.

The start frequency and the sweep range of the sweep unit are adjustable. The start frequency is constant to within 10 Hz over a period of 12 hours and linear in time within the experimental error as measured with the frequency marker unit described below.

In the frequency marker unit the signal of the sweep unit is mixed with a signal controlled by the primary frequency standard. The resulting beat signal is fed to a filter containing a quartz crystal with a very high Q. When the beat frequency equals the resonance frequency of the crystal, a sharp pulse (width about 10 Hz) is generated. By changing the frequency controlled by the frequency standard by 5 kHz very accurate frequency markers are obtained which are fed to the CAT. In this way it is possible to measure the frequency of a transition more accurately than in the conventional manner (Ver 65b). Furthermore, these marker-pulses can also be used to start the CAT, thus completely eliminating the inabilities of the start frequency of the sweep unit mentioned above.

Measurements of the signal to noise ratio as function of time show the validity of the square root law, indicating that correlation effects in the noise are negligible (Ver 65b).

2.4 THE ELECTROMAGNET AND THE NMR PROBE

A commercial Varian V-3501 low-impedance electromagnet is used as the Seeman magnet. The yoke of the magnet is canted 45° to provide good access to the magnetic field region. The pole diameter is 30.3 cm and the gap is 5.0 cm. With these dimensions magnetic field strengths
of up to 12 kG can be attained. The magnet is mounted on a carriage movable a few meters over a pair of rails. It is fed by a regulated Varian V-2500 power supply.

During the experiments the magnetic field strength is monitored by means of a Varian V-8 fluxmeter, which operates on the principle of nuclear magnetic resonance. If the center frequency \( f_0 \) of the nuclear resonance signal is known the value of the magnetic field \( B \) follows from the relation:

\[
B = f_0 \gamma,
\]

(2-1)

where \( \gamma \) is the specific gyromagnetic ratio of the sample. A proton sample (\( \gamma = 4.2578 \text{ MHz/(kG)}^{-1} \)) and a deuteron sample (\( \gamma = 0.6530 \text{ MHz/(kG)}^{-1} \)) are available in cylindrical capsules approximately 6 mm long and 6 mm in diameter. The probe which contains the sample and connects it with the detection system is 16 cm long and 19 mm in diameter. The accuracy of the fluxmeter is determined by the homogeneity of the static magnetic field, the signal to noise ratio, the line width of the nuclear resonance signal, and by the error in the gyromagnetic ratio and in the resonance frequency. By centering accurately the nuclear resonance signal on the scope it is possible (with an obtainable signal to noise ratio of 5) to determine the center of a 0.2 G broad line with an accuracy of about 0.05 G. This results in an accuracy due to the line width of about 2 ppm at 5 kG. However, the gyromagnetic ratio of the proton is known to an accuracy of 13 ppm. The use of a frequency counter (Beezley, Packard 3L 5233) allows measurements of frequency with errors of the order of 1 ppm. Consequently, an overall accuracy of the absolute value of a magnetic field of 5 kG is of the order of 15 ppm if the effects of field inhomogeneities are neglected. Relative measurements can be performed with an accuracy of the order of 1 ppm.

2.5 PERFORMANCE OF THE SPECTROMETER

2.5.1 The sensitivity

The sensitivity of a beam-maser spectrometer is usually expressed as the minimum number of detectable molecules entering the maser cavity for which the corresponding signal to noise ratio equals unity. Theoretical expressions for the sensitivity have been derived by several authors (Gor 55a, Bli 56). Thaddeus and Krisher (Tha 61) discussed the special case of a beam maser spectrometer with a reflection cavity.

Assuming optimum coupling of the cavity the signal to noise ratio (S) to noise (N) ratio for a rotational transition from level \( J \) to level \( J' \) is given by (Tha 61):

\[
\frac{S}{N} = a \frac{n \ h \nu \sin^2(\mu \alpha)}{[P_1 \ kT F \Delta \nu^2]^2},
\]

(2-2)

where \( a \) is a constant depending on the properties of the cavity but independent on molecular parameters; \( \nu \) is the resonance frequency of the rotational transition; \( n = n_i - n_f \), where \( n_i \) and \( n_f \) is the number of molecules in the initial and final state, respectively, of the transition in question passing the cavity per second; \( B \) is the strength of the electric field in the cavity; \( \mu \) is the electric dipole moment matrix element; \( t \) is the transit time of molecules through the cavity; \( P_i \) is the input power to the cavity; \( k \) is Boltzmann's constant; \( T \) is the absolute temperature of the crystal detector; and \( F \) and \( \Delta \nu \) are the overall noise figure and effective bandwidth of the superheterodyne receiver, respectively.

As the electric field \( B \) is proportional to the square root of \( P_i \), the signal to noise ratio increases with monitoring power \( P_i \) until saturation is reached, thereafter the signal to noise ratio decreases with increasing power.

Accurate calculation of the signal to noise ratio of a transition, using Eq.(2-2), is hard to do on account of the complicated action of the state selector. Therefore we shall treat the selection efficiency parametrically. To this end the signal to noise ratio of a given transition without Stark, Zeeman, and hyperfine splitting is compared with the signal to noise ratio of the well measured and strong \( \Delta \nu = \Delta \nu \) transition of HDO. The assumption is made that measurements are performed under identical conditions (\( N_i = N_f \)) with the monitoring power \( P_i \) far below saturation.
Using Eq. (3-2), the ratio of the signal to noise ratios of two transitions can be written as:

\[
\frac{S_i}{S_0} = \frac{S_1}{S_0} \frac{n_1 \hbar v_1 |\mu_{1r}|^2}{n_0 \hbar v_0 |\mu_{0r}|^2},
\]

(2-3)

where \( S \) refers to the \( 2_{e-1} \) transition of HDO and \( 1 \) to the transition in question. If nuclear and spatial degeneracies of the rotational states are included and \( |\mu_{ir}|^2 \) is rewritten (Tov 55, p 97) in terms of rotational line strength, Eq. (2-3) becomes:

\[
\frac{S_i}{S_0} = r \left( \frac{N_i}{N_0} \right) \frac{g_i}{g_0} \frac{f_1}{f_0} \frac{\hbar v_1 |\mu_{1r}|^2}{\hbar v_0 |\mu_{0r}|^2},
\]

(2-4)

where \( r \) represents the ratio of the selection efficiencies of the discussed transitions, \( \frac{N_i}{N_0} \) is the number of molecules passing the cavity per second without state selection, \( g_i/g_0 \) is the statistical weight factor for the rotational level \( i \), \( f_1/f_0 \) represents the fraction of molecules in a rotational state \( i \), \( \hbar v_{1r} \) is the rotational line strength of the involved transition, and \( \mu_{0r} \) is the component of the dipole moment along the \( g \)-axis involved in the transition.

The statistical weight factor in the case of two identical nuclei is explicitly given by Tovess (Tov 55, p 103):

\[
g_i = \frac{2^I I + 1}{2I + 1}, \text{ when the spin function of level } i \text{ is antisymmetric,}
\]

\[
g_i = \frac{2^{I+1}}{2I+1}, \text{ when the spin function of level } i \text{ is symmetric.}
\]

This weight factor is unity in the case of HDO. The fraction of molecules in a particular rotational state \( i \) of an asymmetric top molecule with energy \( \hbar \omega \) is given by (Tov 55, p 101):

\[
f_1 = \frac{e^{-\hbar \omega/\hbar^2}}{\int e^{-\chi/\hbar^2} d\chi},
\]

(2-5)

where \( A, B, \) and \( C \) are the rotational constants given in Table (3-1). The rotational line strengths are listed by Schwendeman and Laurie (Sch 58).

The ratio \( r \) may be calculated from the Stark effect of the involved transitions. However, we feel it more realistic to investigate the relation between \( r \) and the Stark effect empirically. To this end the Stark effect of the transitions listed in Tables 2-1 is calculated from expressions given by Toomes (Tov 55, Ver 60a, Ver 67b, Blu 64, Hos 68). Only these transitions of isotopic species of water were measured with a beam-maser spectrometer while the Zeeman experiments were in progress. The strength of the Stark effect is indicated as good, weak, or very weak according to the expected effectiveness of state selection. The qualification "good" is assigned to the \( 2_{e-2} \) case transition of HDO and "very weak" to the \( 6_{e-5} \) transition of \( \text{H}_2 \text{O}. \) An intermediate case is called "weak". These qualifications are also listed in Table 2-1.

The ratio of the selection efficiencies is easily calculated from the theoretical value of \( S_i/S_0 \) for \( r=1 \) and from the experimental value of \( S_i/S_0 \):

\[
r = \frac{(S_0/S_i)_{exp}}{(S_0/S_i)_{theor, r=1}}.
\]

(2-6)

The results are listed in the eighth column of Table 2-1. This table shows that a weak state selection corresponds to \( r \sim 0.3 \). The \( \text{H}_2 \text{O} \) cavity has a small diameter compared to the \( 2_{e-2} \) cavity of HDO. This decreases the number of molecules contributing to the transition. Taking this into account the "very weak" qualification is estimated to correspond to \( r \sim 0.1 \).

Using the empirical relations between \( r \) and the Stark effect, shown in Table 2-1, the signal to noise ratios for the transitions listed in Table 2-2 are calculated. The results are given in the last column of Table 2-2, showing clearly that these transitions can be measured rather easily.

For practical reasons we decided to measure the \( 7_{e-7} \) transition of HDO, the \( 2_{e-2} \) transition of \( \text{H}_2 \text{O} \), the \( 3_{e-3} \) transition of \( \text{D}_2 \text{O} \), and the \( 6_{e-5} \) transition of \( \text{H}_2 \text{O}. \) The measured signal to noise ratios...
are given in the seventh column of Table 2-3. The good agreement with the semi-theoretical values justifies our approach of the problem and its application in other cases.

The signal to noise ratio of the strongest Zeeman component of a rotational transition is calculated from the experimental signal to noise ratio in the zero field case, using the formulas for the Zeeman intensities given in Sect.3-7. The results, given in the last column of Table 2-3, indicate that the Zeeman effect of the $2_{0^{-2}_{1}}$ transition of HDO and of the $3_{3^{-3}_{2}}$ and $4_{3^{-3}_{2}}$ transitions of D$_2$O can be measured. Preliminary calculations show that the $7_{7^{-7}_{0}}$ transition of DHO in an external magnetic field will probably not be resolved and has a low signal to noise ratio.

The Zeeman effect of the H$_2$O transition is interesting in connection with the isotopic dependence of the magnetic moment tensor. Preliminary calculations indicate a well resolved spectrum, but the low signal to noise ratio requires the application of time averaging techniques.

The Zeeman effect of the HD$^{17}$O transition is not measured in this investigation.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Transition</th>
<th>Number of Zeeman transitions</th>
<th>S/N for the strongest Zeeman component</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDO</td>
<td>$2_{0^{-2}_{1}}$</td>
<td>48</td>
<td>70</td>
</tr>
<tr>
<td>HD$^{17}$O</td>
<td>$7_{7^{-7}_{0}}$</td>
<td>168</td>
<td>0.4</td>
</tr>
<tr>
<td>D$_2$O</td>
<td>$2_{2^{-2}_{1}}$</td>
<td>526</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>32</td>
<td>60</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>$6_{2^{-2}_{1}}$</td>
<td>66</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Table 2-3. Values of the signal to noise ratio for the strongest Zeeman component of several rotational transitions.
2.5.2 Resolving power and stability

The resolving power of the spectrometer is determined primarily by the line width of a transition. At zero magnetic field strength the line width is inversely proportional to the transit time of a molecule through the cavity. The half width is about 1.8 kHz in the experiments with HD, D$_2$O, and H$_2$O using cavities of 16 cm length. The instability of the rubidium frequency standard is better than 5 x 10$^{-11}$. The line broadening due to this instability is negligible.

In addition, a transition in an external magnetic field can further be broadened by inhomogeneities and instabilities of the magnetic field strength.

The homogeneity of the magnetic field in the cavity is measured by means of the NMR probe. To this end, the end caps of the cavity are removed because the diameter of the beam holes is smaller than the outer dimensions of the probe. The magnetic field is also measured in a point just below the cavity outside the vacuum system. This offers a possibility to monitor the magnetic field strength during the experiments. In Fig. 2-4 is shown the relation between the magnetic field in the cavity and at the calibration point for a number of field strengths. The highest magnetic field strength with acceptable inhomogeneities in a cavity 16 cm long is found to be 12 kG (Ver 68d).

Instabilities of the field strength stem from temperature dependent changes in the geometry of the magnet and permeability of iron and in the variation of the line voltage. It is found in practice (Ver 68d) that the magnetic field after a warm-up of four hours is stable enough to neglect the corresponding line broadening.

2.5.3 Illustrative results

Sample averaging techniques turns out to be a very useful and a very reliable extension of the detection system. Weaker details of hyperfine spectra can easily be observed and the hyperfine structure of rotational transitions involving rotational quantum numbers J up to seven are measured and interpreted. Figure 2-5 shows the result of 150 measurements of the central part of the 7$_{1}$-7$_{0}$ transition of HD,
illustrating the possibilities of sample averaging techniques for the resolution of weaker details of the spectrum. With the CAT it is also possible to measure the central line of the $2_2 - 2_1$ transition of HDO without any state selection.

The hyperfine coupling constants of the $6_{1/2} - 5_{1/2}$ transition of HDO are calculated from hyperfine transitions obtained by averaging a part of the hyperfine structure during three days (Ver 66b). This shows clearly good stability of the system.

One of the restrictions of the sample averaging with the CAT is the narrow spectral band width. Only a region of about 100 kHz can be covered by a single scan. By consequence, if the positions of some hyperfine transitions are only roughly known, it takes a long time to scan a broad spectrum.

The high sweep rate of the sweep unit makes it impossible to tune the resonance frequency of the cavity simultaneously. The cavity is therefore adjusted to the center frequency of the scanned part of the spectrum which causes line distortion of the non-central transitions. The corresponding corrections on the frequencies of these transitions are calculated by means of the expressions given by Gordon et al. (Gor 55a).

The described beam-excimer Zeeman spectrometer enables us to measure magnetic splittings of up to 5 MHz without noticeable line broadening at magnetic field strengths up to 12 kOe. A typical observed Zeeman and hyperfine spectrum of the $2_2 - 2_1$ transition of HDO is shown in Fig. 2-6.

The performance of the measuring and monitoring system of the magnetic field strength is best illustrated by comparing the experiments which are performed at different times. Over a period of one year the variation in the frequencies of several Zeeman transitions, measured at magnetic field strength adjusted to the same value, were less than $10^{-4}$ of the Zeeman splittings. These variations lay well within the assumed error in the absolute value for the magnetic field strength as discussed in Sect. 4.4.2 and shows the reliability of the system.
CHAPTER 3

TEUBER

3.1 INTRODUCTION

The hyperfine structure in the rotational spectra of \( ^1\Sigma \) molecule, originating in nuclear spin interactions has been discussed by several authors (Gun 54, Wri 55, Tow 55, Ram 56, Pos 58, Sch 61, Tha 64, Fly 64, Dyn 66, Hui 66, Wac 67, Kim 68). The theory of the Zeeman effect in the rotational spectra of linear and symmetric top molecules was first given by Jen (Jan 51) and by Karrbach and Strandberg (Kah 52). Burke and Strandberg (Bur 53) applied the results of Karrbach and Strandberg to asymmetric top molecules. Ramsey (Ram 52, Ram 56) and Schier (Sch 61) discussed Zeeman effect in the hyperfine spectra of diatomic \( ^1\Sigma \) molecules. Recently Shigenari (Shi 67), Hüttermüller and Polge (Hüt 67), and Neureil (Nue 68) discussed Zeeman effect in the hyperfine spectra of asymmetric top molecules, starting from the Hamiltonian first used by Gunther-Mohr et al (Gun 54) to interpret the hyperfine structure of NH\(_2\). The Stark effect of asymmetric top molecules is well known (Tow 55, p 255); it plays no direct role in beam-maser Zeeman spectroscopy.

The Hamiltonian used for the interpretation of the experimental results is obtained in Sect. 3.2.1 by starting from a general non-relativistic one-particle Hamiltonian as given by Abragam (Abr 57) for the discussion of magnetic shielding effects in nuclear magnetic resonance experiments. The final Stark, Zeeman, and hyperfine Hamiltonians will be given in Sect.3.2.2.

The matrix elements of the Zeeman and hyperfine Hamiltonians for the rotational levels of HCO, HCO, and DCO are given in Sect. 3.3 and 3.4 in terms of J-dependent coupling constants. Matrix elements non-diagonal in the rotational state j, which may accidentally cause sizeable energy splittings, are discussed in Sect. 3.5. Section 3.6 deals with the matrix elements of the hyperfine Hamiltonian for HD\(_{17}\). The relative maser intensities are given in Sect. 3.7.
3.2 THE HAMILTONIAN

3.2.1 The general Stark, Zeeman, and hyperfine Hamiltonian

The Stark, Zeeman, and hyperfine Hamiltonian used for the interpretation of experimental results can be obtained starting from the general non-relativistic classical Hamiltonian for point particles:

\[ H_0 = \sum_q \left( \frac{1}{2m_q} \left( \mathbf{p}_q - e \mathbf{A}_q \right)^2 + \frac{e}{\varepsilon_0} \mathbf{E} \cdot \mathbf{q} \right) + \sum_j \frac{1}{2} \mathbf{p}_{q_j}^2 + \frac{e}{\varepsilon_0} \mathbf{E} \cdot \mathbf{q}_j . \]  

(3-1)

where \( m_q \), \( e \), and \( \mathbf{p}_q \) is mass, charge and momentum respectively, of the \( q \)-th particle, \( \mathbf{A}_q \) and \( \mathbf{E} \) is the vector and the scalar potential, respectively, at the position of the \( q \)-th particle. The summation in Eq. (3-1) extends over all particles (electrons and nuclei) of the molecule. In the following the electronic mass will be denoted by \( m \) and the nuclear masses by \( m_q \).

As we are performing experiments in the laboratory fixed system, it looks appropriate to solve the wave equation corresponding to expression (3-1) in this system. This is generally done by translating Eq. (3-1) to the space fixed molecular CM system and by rotating this system to the principal axes system. The most convenient way, however, is to calculate expression (3-1) in a molecule-fixed frame of reference and to transform the external fields to this coordinate system.

Furthermore we restrict ourselves to \( ^1 \mathrm{I} \) molecules. In this case the spins of electrons couple to a zero total electronic spin. Consequently, effects of electronic spins may be neglected (Gun 54).

The potential \( (\mathbf{A}_q, \phi_q) \) can be written in the molecular frame of reference with external static electric and magnetic fields \( \mathbf{E} \) and \( \mathbf{B} \), respectively, as:

\[ \mathbf{A}_q = \frac{1}{2} \left( \mathbf{E} \cdot \mathbf{r}_q \right) + \frac{e}{\varepsilon_0} \frac{\mathbf{z}_q - \mathbf{E} \cdot \mathbf{z}_q}{r_q^3} , \]

(3-2)

\[ \phi_q = -\mathbf{E} \cdot \mathbf{r}_q + \frac{1}{2} \frac{e}{\varepsilon_0} \frac{z_q - \mathbf{E} \cdot z_q}{r_q^3} . \]

Herein and in the following, the capital subscripts \( K, L \) refer to nuclei and the subscripts \( i, j \) to electrons, the nucleus \( L \) is supposed to have spin \( I_L \) and nuclear magnetic moment \( \gamma_L \mu_N I_L \) where \( \gamma_L \) is the nuclear magneton, \( \mu_N \) represents the Bohr magneton, \( \mathbf{F}_q \) is the position vector of the \( q \)-th particle with respect to the molecular center of mass which can be assumed to be the center of mass of the nuclear frame, \( \mathbf{r}_{pq} = \mathbf{F}_p - \mathbf{F}_q \), and \( \mathbf{r}_{pq} = \mathbf{F}_p - \mathbf{F}_q \).

By substituting expression (3-2) into the expression (3-1) and by writing out the nuclear and electronic terms explicitly we get:

\[ H_0 = h_1 + h_2 + h_3 + h_4 + h_5 + h_6 + h_7 + h_8 , \]

(3-3)

where:

\[ h_1 = \sum_{i} I_i \frac{\mathbf{p}_{i}}{2m} + \sum_{q \neq i} \frac{1}{2} \frac{\mathbf{p}_q^2}{m_q} + \frac{e}{\varepsilon_0} \mathbf{E} \cdot \mathbf{r}_q \]

\[ h_2 = \sum \frac{\mu_N K}{2K} \]

\[ h_3 = -e \sum_{K} K \cdot \mathbf{E}_K \mathbf{E}_K = \sum_{K} \frac{K^2}{2} \]

\[ h_4 = -e \sum_{K} \mathbf{K} \cdot \left( \mathbf{B} - \mathbf{B}_{uu} \right) \mathbf{B} \cdot \mathbf{B} \]

\[ h_5 = \sum \frac{\mu_N K}{2K} \left( \mathbf{r}_K \cdot \mathbf{F}_K \right) \mathbf{r}_K \cdot \mathbf{F}_K \]

\[ h_6 = \sum \frac{\mathbf{B} \cdot \mathbf{F}_K}{2K} \left( \mathbf{B} \cdot \mathbf{F}_K \right) - \sum \frac{\mathbf{F}_K \cdot \mathbf{B} \cdot \mathbf{F}_K}{2K} \]

\[ h_7 = \sum \frac{\mathbf{B} \cdot \mathbf{F}_K}{2K} \left( \mathbf{F}_K - \mathbf{F}_K \right) \cdot \left( \mathbf{B} \cdot \mathbf{F}_K \right) \]

\[ h_8 = \sum \frac{\mathbf{F}_K \cdot \mathbf{B} \cdot \mathbf{F}_K}{2K} \]
The terms $h_1$ and $h_2$ represent the molecular Hamiltonian if there are no external fields, and contributions of electronic and nuclear spins are neglected. Solution of the wave equation in this case gives the rovibronic (rotational-vibrational-electronic) wave function $\psi_{\text{evr}}$ and the corresponding energy levels. In the Born Oppenheimer approximation the rovibronic wave function can be written as a product of an electronic wave function $\psi_e$ and a vibrational wave function $\psi_v$ (Run 68). If we neglect the vibrational angular momentum the rovibronic wave function can be written as a product of a rotational $\psi_r$ and a vibrational wave function $\psi_v$. Consequently:

$$\psi_{\text{evr}} = \psi_e \psi_v \psi_r \psi_v^* \psi_r^*$$ \hspace{1cm} (3-4)

The electronic state is generally denoted by $|\psi_e\rangle$ and the corresponding eigenvalues by $E_e$. The electronic ground state with energy $E_e$ will be denoted by $|\phi_e\rangle$. The rotational and vibrational states are denoted by $|r\rangle$ and $|v\rangle$, respectively, with corresponding eigenvalues $E_r$ and $E_v$.

Usually one neglects the vibrational effects in first approximation and assumes a rigid molecular frame. So far, this rigid rotor model turned out to be adequate for the interpretation of hyperfine (Run 67, 67a) and Zeeman splittings (Run 53) of the rotational transitions of water.

In the rigid rotor model the term $h_2$ can be written as (Wil 55):

$$h_2 = \frac{\alpha}{2\hbar^2} \sum_{i \neq j} \left( R_{ij}^2 \right) \frac{\mu_{ij}}{R_{ij}^3} \left( \tilde{F}_{ij}^2 \left( \tilde{R}_{ij}^2 \right) \right)$$

$$= \frac{\alpha}{2\hbar^2} \sum_{i \neq j} \left( R_{ij}^2 \right) \frac{\mu_{ij}}{R_{ij}^3} \left( \tilde{F}_{ij}^2 \left( \tilde{R}_{ij}^2 \right) \right)$$

$$= \frac{\alpha}{2\hbar^2} \sum_{i \neq j} \left( R_{ij}^2 \right) \frac{\mu_{ij}}{R_{ij}^3} \left( \tilde{F}_{ij}^2 \left( \tilde{R}_{ij}^2 \right) \right)$$

$$= \frac{\alpha}{2\hbar^2} \sum_{i \neq j} \left( R_{ij}^2 \right) \frac{\mu_{ij}}{R_{ij}^3} \left( \tilde{F}_{ij}^2 \left( \tilde{R}_{ij}^2 \right) \right)$$

(3-5)

where $N$ is the total angular momentum of the nuclei, $A_g$ is the rotational constant, and $g = a, b, c$ stands for one of the principal axes of the molecule. By writing the total angular momentum $\mathbf{J}$ as the sum:

$$\mathbf{J} = N + \mathbf{L}$$ \hspace{1cm} (3-6)

of rotational and electronic angular momentum $\mathbf{L}$, and noting that $\mathbf{J}$ and $\mathbf{L}$ commute in a molecule fixed coordinate system, expression (3-5) becomes:

$$\sum_{g} A_g \mathbf{g}^2 = \sum_{g} \left( A_g \mathbf{g}^2 = 2A_g \mathbf{J}_g \mathbf{L}_g + A_g \mathbf{L}_g^2 \right)$$ \hspace{1cm} (3-7)

The first terms of the right side of Eq. (3-7) represents the unperturbed rigid rotor Hamiltonian with states $|100\rangle$ and eigenvalues $A_g \mathbf{g}^2$. The term $2 \sum_{g} A_g \mathbf{g}^2 \mathbf{L}_g$ can be considered as a perturbation which excites electrons from the $|1\rangle$ state to $|1\rangle$ states. The last term of Eq. (3-7) is independent on the rotational state and does not contribute to splitting of the energy levels.

The interaction of the molecular electronic and nuclear charges with the external electric field is given in $h_4$ of Eq. (3-3).

By expressing the linear momentum in terms of the angular momentum and noting that $\mathbf{L}$ and $\mathbf{J}$ do not commute in the molecule fixed system, the nuclear contribution $h_4^N$ to $h_4$ may be written as:

$$h_4^N = \frac{\mu}{\hbar} \sum_{k} \left( \tilde{R}_{ik}^2 \tilde{R}_{ik} + \tilde{S}_{ik} \tilde{S}_{ik} \right)$$

$$= \frac{\mu}{\hbar} \sum_{k} \left( \tilde{R}_{ik}^2 \tilde{R}_{ik} + \tilde{S}_{ik} \tilde{S}_{ik} \right)$$

$$= \frac{\mu}{\hbar} \sum_{k} \left( \tilde{R}_{ik}^2 \tilde{R}_{ik} + \tilde{S}_{ik} \tilde{S}_{ik} \right)$$

$$= \frac{\mu}{\hbar} \sum_{k} \left( \tilde{R}_{ik}^2 \tilde{R}_{ik} + \tilde{S}_{ik} \tilde{S}_{ik} \right)$$

$$= \frac{\mu}{\hbar} \sum_{k} \left( \tilde{R}_{ik}^2 \tilde{R}_{ik} + \tilde{S}_{ik} \tilde{S}_{ik} \right)$$

$$= \frac{\mu}{\hbar} \sum_{k} \left( \tilde{R}_{ik}^2 \tilde{R}_{ik} + \tilde{S}_{ik} \tilde{S}_{ik} \right)$$

(3-8)
with \( q_{a}^{(n)} = \frac{\mu_{B}}{h} A_{a} \cdot E_{K} \left[ f_{H}^{(i)}(s_{a}, s_{a}) - \left( \frac{r_{L}}{r_{K}} \right) f_{H}^{(i)}(s_{a}, s_{a}) \right] \)

and \( q_{a}^{(n)} = q_{a}^{(n)\ast} \) in \( 66^{\prime} \).

In the last step leading to Eq. (3-8) use is made of the relation

\[
\omega_{a} = \frac{E_{a} - A_{a}}{A_{a}} ,
\]

which is valid in the principal axes system.

By substituting the total angular momentum \( J = 66 + L \) and writing the results as a product of Cartesian tensors according to:

\[
\Xi_{a}^{(n)} = \frac{A_{a}^{(n)}}{A_{a}} ,
\]

we get for Eq. (3-8):

\[
h_{n}^{(n)} = \omega_{a} \Xi_{a}^{(n)} - \Xi_{a}^{(n)} \omega_{a} ,
\]

In a similar way the electronic contribution \( h_{n}^{e} \) to \( h_{n} \) is shown to be (Ver 66):

\[
h_{n}^{e} = \omega_{a} \Xi_{a}^{(n)} .
\]

As \( \omega_{a} \to 0 \), the last two terms of Eq. (3-10) are negligible and \( h_{n} \) can be written as:

\[
h_{n} = -\omega_{a} \Xi_{a}^{(n)} - \omega_{a} \Xi_{a}^{(n)} .
\]

The remaining term of \( h_{n} \) contributes to the spin-rotation interaction \( h_{n} \). The complete expression for this interaction is (Fyi 66, Byn 66):

\[
h_{n} = \sum_{K} \left[ h_{n}^{(K)}(s_{a}, s_{a}) - \left( \frac{r_{L}}{r_{K}} \right) h_{n}^{(K)}(s_{a}, s_{a}) \right] .
\]

As shown by Ramsey (Nam 56) the energy of this interaction lies well below the resolving power of a beam maser spectrometer.

The electronic contribution to the term \( h_{n} \) of Eq. (3-3) represents the response of the electronic charge distribution to the external magnetic field. The interaction of the resulting induced magnetic moment with the external magnetic field is given by:

\[
h_{n} = \frac{\mu_{B}}{h} \sum_{K} \left[ f_{H}^{(n)}(s_{a}, s_{a}) - \left( \frac{r_{L}}{r_{K}} \right) f_{H}^{(n)}(s_{a}, s_{a}) \right] .
\]

In addition the electronic charge distribution will shield the nuclear magnetic moment from the external B-field. This effect is described by the second term of \( h_{n} \), which may be written as:

\[
h_{n} = \sum_{K} \left[ h_{n}^{(K)}(s_{a}, s_{a}) - \left( \frac{r_{L}}{r_{K}} \right) h_{n}^{(K)}(s_{a}, s_{a}) \right] .
\]

The complete expression for the interaction is (Byn 66, Byn 66):

\[
h_{n} = \sum_{K} \left[ h_{n}^{(K)}(s_{a}, s_{a}) - \left( \frac{r_{L}}{r_{K}} \right) h_{n}^{(K)}(s_{a}, s_{a}) \right] .
\]

where \( h_{n}^{(K)}(s_{a}, s_{a}) \) is given by:

\[
h_{n}^{(K)} = \left[ h_{n}^{(K)}(s_{a}, s_{a}) - \left( \frac{r_{L}}{r_{K}} \right) h_{n}^{(K)}(s_{a}, s_{a}) \right] .
\]

As shown by Ramsey (Nam 56) the energy of this interaction lies well below the resolving power of a beam maser spectrometer.
\[ M'(K) \equiv M(K) \cdot \]
\[ M'(K) \equiv M(K) \cdot 
\]
\[ \frac{\nu}{\hbar} \cdot \left[ \int \mathbf{r}_K \cdot \left( \mathbf{T}_L^2 \mathbf{S}_L^2 \mathbf{S}_L \right) - \left( \mathbf{T}_L^2 \mathbf{S}_L \right) \right] \cdot \]
\[ M'(K) \equiv M(K) \cdot \]
\[ \gamma = \frac{1}{2} \cdot \frac{Z_{\pi} M}{E_p K} \cdot \]

and \( m_p \) is the proton mass.

The terms of the expression (3-15) missing in \( h_3 \) cannot be obtained with the present approach starting from Eq. (3-1). These terms can be obtained by defining Eq. (3-1) in the space-fixed system and applying a transformation to the molecule-fixed system, taking into account relativistic effects (Wac 67). They can also be obtained by calculating the magnetic field at the \( K \)-th nucleus produced by other molecular charge carriers and transforming the resulting expression to the molecular CN system (ijn 66).

In the present approach the nuclei are assumed to be point charges. In consequence, the Hamiltonian (3-1) does not contain direct interactions involving nuclear electric quadrupole moments and nuclear magnetic moments. Interactions due to higher order nuclear moments can be neglected because all nuclei of the molecules discussed in this investigation have spins less than 3/2.

The interaction of the electric quadrupole moment of the \( K \)-th nucleus with the electric field gradient due to the surrounding electronic and nuclear charges can be written as the scalar product of two spherical tensor operators (Ehm 60):

\[ H'_{KL} = Q^{(2)}_{KL} \cdot Q^{(2)}_{KL} \cdot (3-15) \]

with \( Q^{(2)}_{KL} = \sum_p e_p \cdot \mathbf{P}_{FK}^{(2)}(0_{FK}, \mathbf{r}_K) \).

\[ v^{(2)}_{KL} \equiv \sum_p e_p \cdot \mathbf{P}_{FK}^{(2)}(0_{FK}, \mathbf{r}_K). \]

The first summation extends over all protons of the \( K \)-th nucleus, \( (0_{FK}, \mathbf{r}_K) \) are the polar angles of the radius vector \( \mathbf{r}_K \), and the components of the spherical tensor \( c^{(2)} \) are defined in the reference cited.

The nuclear magnetic moments contribute in two ways to the Hamiltonian:

\[ H_{LL} = \sum_{KL} P_{KL}^{(2)} \mathbf{S}_L \cdot \mathbf{S}_L \cdot (3-16) \]

and \( H_{LL} = \sum_{KL} \mathbf{S}_L \cdot \mathbf{S}_L \cdot (3-16) \)

with \( P_{KL}^{(2)} = \sum_p e_p \cdot \mathbf{P}_{FK}^{(2)}(0_{FK}, \mathbf{r}_K) \).

The first term of Eq. (3-16) represents the classical interaction between two nuclear magnetic dipole moments. The second term is the Zeeman energy of the nuclear magnetic moments in the external field \( \mathbf{B} \).

Consequently the non-negligible terms to the unperturbed Hamiltonian can be extracted from expressions (3-7), (3-11) through (3-16), and \( h_3 \) of (3-3):

\[ H' = H'_{KL} + \cdot (3-17) \]

where

\[ H'_{KL} = -e \cdot \sum_{KL} \mathbf{F}_K \cdot \mathbf{S}_L \cdot \mathbf{S}_L + c \cdot \sum_{KL} \mathbf{F}_K \cdot \mathbf{S}_L \cdot \mathbf{S}_L + \sum_p e_p \cdot \mathbf{P}_{FK}^{(2)}(0_{FK}, \mathbf{r}_K) \cdot \mathbf{S}_L \cdot \mathbf{S}_L \cdot \mathbf{B} \]

with \( \sum_p e_p \cdot \mathbf{P}_{FK}^{(2)}(0_{FK}, \mathbf{r}_K) \cdot \mathbf{S}_L \cdot \mathbf{S}_L \cdot \mathbf{B} \).
This Hamiltonian can be written for the electronic ground state in terms of operators which operate only on nuclear and rotational variables by application of perturbation theory with respect to the electronic states:

\[ H_n = \langle 0 | H_n^e | 0 \rangle + \frac{\langle 0 | S^{a(4)} | n \rangle - \langle 0 | S^{a(4)} | n \rangle}{n \neq 0 \neq n} + \cdots. \quad (3-18) \]

The first order term can be written in the same form as \( H_1 \) of Eq. (3-17) if the electronic operators are replaced by their expectation values in the electronic ground state. For example, the diamagnetic susceptibility term becomes:

\[ \frac{1}{2} \langle 0 | S^{a(4)} | S^{a(4)} \rangle \text{ with } \langle 0 | \chi(a) | 0 \rangle \text{ now replaced by } \langle 0 | \chi(a) | 0 \rangle. \]

The contribution of \( H_1 \) and the mixed contributions of \( H_1 \) and \( H_2 \) to the second order term of Eq. (3-18) are negligible at low external electric fields. The contribution of the terms of \( H_2 \) to the first order term of Eq. (3-18) is either zero or can be neglected (see 66). However, these terms have important second order contributions:

\[
\sum_{n \neq 0} \frac{\langle 0 | F_{1n}^{(e)} | n \rangle - \langle 0 | F_{1n}^{(e)} | n \rangle}{n \neq 0} = \sum_{n \neq 0} \frac{\langle 0 | F_{1n}^{(e)} | n \rangle - \langle 0 | F_{1n}^{(e)} | n \rangle}{n \neq 0} + \cdots.
\]

The first term of Eq. (3-19) can be neglected since it represents only a very small correction to the rotational constants and to the direction of the principal axes. The following terms are contributions of the excited electronic states to the molecular magnetic moment, to the magnetic susceptibility, to the spin-rotation interaction, to the nuclear magnetic shielding, and to the indirect nuclear spin-spin...
interaction, respectively. As discussed above the last term can be neglected in the case of beam-passer spectroscopy. The contributions of \( \mathcal{H}_1 \) and the mixed contributions of \( \mathcal{H}_2 \) and \( \mathcal{H}_3 \) to the second order term of Eq. (3-18) are negligible at low external electric fields.

The total Stark, Zeeman and hyperfine Hamiltonian in terms of nuclear and rotational operators is the sum of the first order terms of \( \mathcal{H}_1 \) of Eq. (3-17) and of the second order terms of \( \mathcal{H}_2 \) given in expression (3-19):

\[
\mathcal{H}'' = \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_{\text{hyp}}\]

(3-20)

with:

\[
\mathcal{H}_2 = \mathcal{H}_0 \left[ \mathcal{H}^{(n)}_0 \mathcal{H}^{(s)}_0 \right] + \mathcal{J} \cdot \mathcal{J} \cdot \mathcal{H}^{(n)}_0 \mathcal{H}^{(s)}_0)
\]

where

\[
\mathcal{H}_0 = -\mathcal{H}_0 \left[ \mathcal{H}^{(n)}_0 \mathcal{H}^{(s)}_0 \right] \mathcal{J} \cdot \mathcal{J} \cdot \mathcal{H}^{(n)}_0 \mathcal{H}^{(s)}_0)
\]

\[
\mathcal{H}_{\text{hyp}} = \mathcal{H}_{\text{hyp}} \left[ \mathcal{H}^{(n)}_{\text{hyp}} \mathcal{H}^{(s)}_{\text{hyp}} \right] \mathcal{J} \cdot \mathcal{J} \cdot \mathcal{H}^{(n)}_{\text{hyp}} \mathcal{H}^{(s)}_{\text{hyp}})
\]

The matrix elements of \( \mathcal{H}_{\text{hyp}} \) and \( \mathcal{H}_2 \) diagonal in the rotational quantum numbers \( J \) are important (Ver 68a). With group theoretical arguments one can show (Sect. 3-3) that only diagonal components of the relevant interaction tensors contribute to these matrix elements. This enables us to simplify the Hamiltonian given in Eq. (3-20). By expressing \( \mathcal{J} \) and \( \mathcal{J}_0 \) as occurring in the spin-rotation and the magnetic shielding tensor in the coordinate system with the origin at the K-th nucleus (Fly 66, Fly 69, Neu 68) the effective total Hamiltonian is:

\[
H_{\text{eff}} = \sum_{\text{K} \text{L}} \mathcal{H}_{\text{K}}^{(n)} \mathcal{H}_{\text{K}}^{(s)} + \frac{1}{2} \left[ \mathcal{H}_{\text{K}}^{(n)} \mathcal{H}_{\text{K}}^{(s)} + \mathcal{H}_{\text{K}}^{(s)} \mathcal{H}_{\text{K}}^{(n)} \right]
\]

(3-21)

with:

\[
\mathcal{H}_{\text{K}}^{(n)} = \mathcal{H}_{\text{K}}^{(n)}(e) + \mathcal{H}_{\text{K}}^{(n)}(p),
\]

\[
\mathcal{H}_{\text{K}}^{(s)} = \mathcal{H}_{\text{K}}^{(s)}(e) + \mathcal{H}_{\text{K}}^{(s)}(p),
\]

\[
\mathcal{H}_{\text{K}} = \mathcal{H}_{\text{K}}^{(n)} + \mathcal{H}_{\text{K}}^{(s)}.
\]

Herein, \( \mathcal{H}_{\text{K}} = \mathcal{H}_{\text{K}}^{(n)} + \mathcal{H}_{\text{K}}^{(s)} \) is the molecular electric dipole moment.

In contrast to the Zeeman and Hyperfine Hamiltonian given by several authors (Fly 66a, Hui 66, Shi 67, Bux 68, Neu 68), the Hamiltonian given in expression (3-20) is hermitian, as it of course, should be.

### 3.2.2 The effective Hamiltonian

For the rotational levels involved in this investigation only the
matrix elements of expression (3-21) is the space fixed ON system. For this reason the Hamiltonian (3-20) is transformed from the molecule fixed to the space fixed ON system.

3.3 MATRIX ELEMENTS OF \( H_{\text{hyp}} \) AND \( E_2 \) FOR HDO

At high magnetic fields, such that the Zeeman energy is much larger than hyperfine energy, the coupling between \( J \), \( I_d \), and \( I_H \) is broken down. In this case the most appropriate representation will be:

\[
|JnM_J,M_N,M_h\rangle, \text{ abbreviated as } |nM_J\rangle.
\]

If the space fixed \( z \)-axis is chosen along the positive direction of the external magnetic field then only \( M_h = M_J = M \) will be a good quantum number.

Apart from the quadrupole term, expression (3-21) consists of terms of the form \( \hat{A}_0 \hat{F}, \hat{F}_0 \), where \( \hat{A} \) and \( \hat{F} \) is one of the vector operators \( \hat{I}_p, \hat{I}_q, \hat{I}_r \) or \( \hat{S} \), and \( \hat{F} \) is a second rank tensor depending explicitly on molecular properties. To calculate the matrix elements of expression (3-21), the operator \( \hat{A}_0 \hat{F}, \hat{F}_0 \) is expanded in spherical components as (Hui 66):

\[
\hat{A}_0 \hat{F} = \sum_{l=0,1,2} (-1)^{2l+1} \frac{1}{2l+1} \sum_{m=-l}^l \hat{A}_m^{(l)} \hat{F}_m^{(l)} |l,m\rangle.
\]

where the spherical components of \( \hat{a}^{(l)} \), in terms of the Cartesian components, are given by (Yut 68, p 106):

\[
\hat{a}_0^{(l)} = \delta_{l0} \frac{1}{2} (\hat{T}_{xx} + \hat{T}_{yy} + \hat{T}_{zz}) ,
\]

\[
\hat{a}_1^{(l)} = \frac{1}{2} \left( \hat{T}_{yx} \hat{T}_{xy} - \hat{T}_{xy} \hat{T}_{yx} \right) ,
\]

\[
\hat{a}_2^{(l)} = \frac{1}{2} \left( \hat{T}_{x} \hat{T}_{x} \hat{T}_{y} \hat{T}_{y} \hat{T}_{z} \hat{T}_{z} \right) ,
\]

with \( \hat{T}_{ij} = T_{ij} \hat{F}_i \hat{F}_j \).
The reduced matrix elements of Eq. (3-24) can be evaluated with the aid of the Wigner-Eckart theorem. The reduced matrix of the interaction tensors are written in terms of molecular constants by transforming \( \mathbf{\hat{q}} \) from the space-fixed to the molecule-fixed CM system and by expanding the asymmetric rotor wave function as a linear combination of symmetric top functions \((\text{Hui} 66)\). The resulting relations are:

\[
\langle J\sigma \mathbf{q} \rangle \left| \langle J\sigma \mathbf{q} \rangle \right| J \rangle = \left( \frac{2J+1}{3} \right) \langle \mathbf{d} \mathbf{a} \mathbf{b} \mathbf{c} \rangle,
\]

\[
\langle J\sigma \mathbf{q} \rangle \left| \langle J\sigma \mathbf{q} \rangle \right| J \rangle = \delta
\]

(3-25)

Using tensor operator techniques (Judd 63, Chap 3), the matrix elements can then be written in terms of magnetic field strength, the nuclear and rotational quantum numbers, and the reduced matrix elements of \( \mathbf{a} \), \( \mathbf{b} \) and \( \mathbf{c} \). The quadrupole term can be evaluated in a similar manner.

For example, the matrix element of \( \mathbf{\hat{B}} \cdot \mathbf{\hat{J}} \), diagonal in \( J \), can be evaluated in the \( |M_a^a, M_b^b, M_c^c \rangle \) representation as:

\[
\langle J\sigma \mathbf{q} \rangle \left| \langle J\sigma \mathbf{q} \rangle \right| J \rangle = \sum_{M_a^a, M_b^b, M_c^c} \left( -1 \right)^{J_a + J_b - M_a} \left( \frac{2J+1}{3} \right) \langle J\sigma \mathbf{q} \rangle \left| \langle J\sigma \mathbf{q} \rangle \right| J \rangle = \sum_{M_a^a, M_b^b, M_c^c} \left( -1 \right)^{J_a + J_b - M_a} \left( \frac{2J+1}{3} \right) \langle J\sigma \mathbf{q} \rangle \left| \langle J\sigma \mathbf{q} \rangle \right| J \rangle
\]

(3-23)

Using the expression for the sum over 3-j symbols given by Judd (Judd 63, p. 57) the expression for the matrix element can be written as:

\[
\langle J\sigma \mathbf{q} \rangle \left| \langle J\sigma \mathbf{q} \rangle \right| J \rangle = \sum_{M_a^a, M_b^b, M_c^c} \left( -1 \right)^{J_a + J_b - M_a} \left( \frac{2J+1}{3} \right) \langle J\sigma \mathbf{q} \rangle \left| \langle J\sigma \mathbf{q} \rangle \right| J \rangle = \sum_{M_a^a, M_b^b, M_c^c} \left( -1 \right)^{J_a + J_b - M_a} \left( \frac{2J+1}{3} \right) \langle J\sigma \mathbf{q} \rangle \left| \langle J\sigma \mathbf{q} \rangle \right| J \rangle
\]

(3-24)

By an analogue treatment, the final expression for the diagonal matrix elements in terms of \( n \)-j symbols (Not 59) and the coupling constants defined in Table 3-2 is (Ver 67e):

\[
\langle J\sigma \mathbf{q} \rangle \left| \langle J\sigma \mathbf{q} \rangle \right| J \rangle = \sum_{M_a^a, M_b^b, M_c^c} \left( -1 \right)^{J_a + J_b - M_a} \left( \frac{2J+1}{3} \right) \langle J\sigma \mathbf{q} \rangle \left| \langle J\sigma \mathbf{q} \rangle \right| J \rangle = \sum_{M_a^a, M_b^b, M_c^c} \left( -1 \right)^{J_a + J_b - M_a} \left( \frac{2J+1}{3} \right) \langle J\sigma \mathbf{q} \rangle \left| \langle J\sigma \mathbf{q} \rangle \right| J \rangle
\]

(3-25)
### Table 3-2: Hyperfine and magnetic coupling constants

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_{ij}$</td>
<td>$\chi_{ij} = \frac{1}{2} x_{ij}$</td>
</tr>
<tr>
<td>$\chi_{ij}$</td>
<td>isotropic part of the molecular magnetic susceptibility</td>
</tr>
<tr>
<td>$\chi_{ij}^{(0)}$</td>
<td>anisotropic part of the molecular magnetic susceptibility</td>
</tr>
<tr>
<td>$q_i$</td>
<td>nuclear quadrupole moment</td>
</tr>
<tr>
<td>$g_i$</td>
<td>K-th quantum number</td>
</tr>
<tr>
<td>$c_i^0$</td>
<td>nuclear spin-spin</td>
</tr>
<tr>
<td>$c_i^1$</td>
<td>quadrupole moment of the nucleus</td>
</tr>
<tr>
<td>$c_i^2$</td>
<td>quadrupole moment of the nucleus</td>
</tr>
<tr>
<td>$c_i^3$</td>
<td>quadrupole moment of the nucleus</td>
</tr>
<tr>
<td>$c_i^4$</td>
<td>quadrupole moment of the nucleus</td>
</tr>
</tbody>
</table>

### Mathematical Expressions

\[
\chi = \frac{1}{2} x_{ij}
\]

\[
q_i = 2 g_i \mu_B E_i
\]

\[
\frac{\partial}{\partial \mu_B} \chi_{ij} = x_{ij} \frac{\partial \chi_{ij}}{\partial \mu_B}
\]

\[
\chi_{ij} = \frac{1}{2} x_{ij}
\]

\[
q_i = 2 g_i \mu_B E_i
\]

\[
x_{ij} = \frac{1}{2} x_{ij}
\]

\[
\frac{\partial}{\partial \mu_B} \chi_{ij} = x_{ij} \frac{\partial \chi_{ij}}{\partial \mu_B}
\]
3.4 THE MATRIX ELEMENTS OF $H_{\text{hyd}}$ AND $H_{z}$ FOR $D_2O$ AND $H_2O$

Interchange of the two equivalent deuterons in $D_2O$ must leave the total wave function unchanged. On the other hand, the total wave function of $H_2O$ must be antisymmetric with respect to an interchange of the two protons. In consequence, the total nuclear spin $I_{1}+I_{2}$ can take only definite even or odd values depending on the interchange symmetry of the rotational state. This symmetry argument also holds in an external magnetic field.

So when the Zeeman energy exceeds the hyperfine energy, the coupling between $j$ and $I$ is broken down and $|JM_{I},JM_{I','I}\rangle$ is the most convenient representation. In this representation $I_{1}+I_{2}$ commutes with the Hamiltonian, i.e., $H_{Z}=HM_{I}$ is a good quantum number.

By a treatment analogous to that of the preceding section the matrix elements of $H_{\text{hyd}}$ and $H_{z}$ can be evaluated (Var 68):

$$\langle J;M_{J},I_{1},I_{2},I_{1}';I_{2}' | H_{\text{hyd}} + H_{z} | J;M_{J},I_{1},I_{2},I_{1}';I_{2}' \rangle =$$

$$-\frac{1}{2} \sum_{q} J_{q}^{2} \left[ J_{q}^{2} + J_{q}^{2} - M_{J}M_{J,'} \right] \left[ (2J_{q}+1)(2J_{q}+1)(2J_{q}+1)(2J_{q}+1) \right] \delta(J_{q}+1) \delta(J_{q}) \times$$

$$x \delta_{M_{J},M_{J},'}, \delta_{I_{1},I_{1}'+1}, \delta_{I_{1},I_{1}'} \delta(J_{q}+1) \delta(J_{q})$$

$$+ \epsilon_{\text{K}} \left[ (-)^{M_{J}+M_{J,'}+J_{q}} \right] \frac{1}{4} \sum_{q} J_{q}^{2} \left[ J_{q}^{2} + J_{q}^{2} - M_{J}M_{J,'} \right] \left[ (2J_{q}+1)(2J_{q}+1)(2J_{q}+1)(2J_{q}+1) \right] \delta(J_{q}+1) \delta(J_{q})$$

$$x \delta_{M_{J},M_{J},'}, \delta_{I_{1},I_{1}'+1}, \delta_{I_{1},I_{1}'}$$

$$+ \frac{1}{2} \sum_{q} J_{q}^{2} \left[ J_{q}^{2} + J_{q}^{2} - M_{J}M_{J,'} \right] \left[ (2J_{q}+1)(2J_{q}+1)(2J_{q}+1)(2J_{q}+1) \right] \delta(J_{q}+1) \delta(J_{q})$$

$$x \delta_{M_{J},M_{J},'}, \delta_{I_{1},I_{1}'+1}, \delta_{I_{1},I_{1}'}$$

$$\times \left[ \frac{(2J_{q}+1)(2J_{q}+1)(2J_{q}+1)(2J_{q}+1)}{2J_{q}+1} \right] \left[ \frac{(2J_{q}+1)(2J_{q}+1)(2J_{q}+1)(2J_{q}+1)}{2J_{q}+1} \right] \delta(J_{q}+1) \delta(J_{q})$$

$$\times \delta_{I_{1},I_{1}'+1}, \delta_{I_{1},I_{1}'} \delta(J_{q}+1) \delta(J_{q})$$

3.5 SECOND-ORDER EFFECTS WITH RESPECT TO THE ROTATIONAL STATE

The second-order contribution of the perturbation given in Eq. (3-20) to the energy of the state $|e,J,M,I\rangle$, where $e$ represents the nuclear quantum numbers, is given by the standard perturbation formula:

$$\delta E_{J,M,I} = \sum \frac{1}{2} \left[ \frac{|e,J,M,I\rangle \langle e,J',M',I'|}{W_{J,M,I} - W_{J',M',I'}} \right]^{2}$$

Among the terms of Eq. (3-20) the linear Zeeman term is by far the strongest one in an external magnetic field. By consequence, the second order contribution of this term, which is proportional to $B_{z}^{2}$, is likely to be the leading correction. Fortunately this contribution, and hence also of other second order terms, can be neglected for the levels of $D_{2}O$, $D_{2}O$ and $H_{2}O$ involved in this investigation (Var 68c).

There is another effect producing contributions to the energy proportional to $B_{z}^{2}$ in the laboratory fixed coordinate system there is only an external magnetic field $B_{z}$ and no electric field $E$. However, a molecule travelling with a velocity $\vec{v}$ in a magnetic field "sees"
also an electric field because of relativity effects. Defining $B_y$, $E_y$, and $B_z$, $E_z$ as the components of $\mathbf{B}$ and $\mathbf{E}$ parallel and perpendicular to the molecular velocity $\mathbf{v}$, respectively, a transformation from the space-fixed to the molecular center of mass system yields (Van 56, p 330):

\begin{align}
B_y' &= B_y, \\
E_y' &= 0, \\
B_z' &= B_z(1-v^2/c^2)^{1/2} + E_z, \\
E_z' &= (\mathbf{\nabla} \times \mathbf{B})(1-v^2/c^2)^{1/2} = \mathbf{\nabla} \times \mathbf{E},
\end{align}

(5-30)

where $\mathbf{E}'$, $\mathbf{B}'$ are the magnetic and the electric field strength, respectively, in the molecular frame of reference. With $\mathbf{B}$ directed along the z-axis and $\mathbf{v}$ along the x-axis, the Hamiltonian for the interaction of the molecule with the electric field $\mathbf{E}'$ is given by (Eq. 3-20):

\[
H_B = -\mathbf{\nabla}\cdot\mathbf{E}' + \gamma_0 \mathbf{B}'.
\]

(3-31)

At 12 kHz and room temperature this interaction is about 100 Hz, and may be considered as a perturbation on $H_0 = H_0 + H_{\text{DPD}} + H_{\text{J}}$ with eigenvalues $\omega_{\text{J}}$ at J. At this magnetic field strength $H_B$ is much larger than $H_{\text{DPD}}$, and the eigenfunctions of $H_B$ may be approximated to be $|\omega_{\text{J}}\rangle$.

As can be seen by group theoretical arguments (Van 56) the first order contribution of (3-31) is zero in the case of an asymmetric rotor.

The second-order contributions can be written as:

\[
\Delta H_{\text{J}} = \sum_{\text{M}} \psi_{\text{JM}}^* \psi_{\text{J'}} \psi_{\text{M'}} \psi_{\text{J'}} \psi_{\text{M'}}
\]

with $\psi_{\text{JM}} = \psi_{\text{J'M'}} \times \psi_{\text{JM}}$.

By referring $\psi_{\text{J}}$ to the spherical basis we obtain from Eq. (3-26) with standard tensor operator techniques (Ver 68c):

\[
\Delta H_{\text{J}} = \sum_{\text{M}} \psi_{\text{JM}}^* \psi_{\text{J'}} \psi_{\text{M'}} \psi_{\text{J'}} \psi_{\text{M'}}
\]

where $\psi_{\text{J',M'}}$ are the tabulated rotational line strengths (Sch 58) and $\nu_{\text{g}}$ the g-th component of the molecular electric dipole moment.

Explicit expressions of the induced Stark effect given in Eq. (3-32) are listed in Table 3-3 for a number of levels of HDO and D$_2$O. As can be seen from this Table, the effect of molecular velocity must be taken into account in the case of HDO but can safely be neglected for the levels of D$_2$O.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Rotational level</th>
<th>Induced Stark effect</th>
<th>Induced Stark effect at 12 kHz and 625 m/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDO</td>
<td>2</td>
<td>(3.66-0.60)\nu B</td>
<td>(205-304) Hz</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>(-3.60+0.55)\nu B</td>
<td>(-205+334) Hz</td>
</tr>
<tr>
<td>D$_2$O</td>
<td>2</td>
<td>(-0.45-0.06)\nu B</td>
<td>(-26-34) Hz</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>(0.46+0.05)\nu B</td>
<td>(9.4+2.8) Hz</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>(0.30+0.01)\nu B</td>
<td>(17+0.6) Hz</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>(-0.13-0.01)\nu B</td>
<td>(-7.1-0.7) Hz</td>
</tr>
</tbody>
</table>

Table 3-3. The induced Stark effect of a number of HDO and D$_2$O levels.
3.6 MATRIX ELEMENTS OF $H_{\text{np}}$ FOR HD$^{17}$O

The appropriate coupling scheme for HD$^{17}$O in the absence of external fields is:

$$J + I_0 = F_1,$$

$$F_1 + T_D = F_2,$$

$$F_2 + T_H = F.$$

With $I_0 = 5/2$, $I_D = 1$ and $I_H = 1$, the rotational $J = 2$ level will be split into 28 hyperfine levels. The matrix elements of the several hyperfine interactions diagonal in the rotational state, are evaluated in the representation $|J;F_1,F_2,F_H,F_D,\mathbf{M}_H,\mathbf{M}_D\rangle$, in the following abbreviated as $|J;F_1,F_2,F_H,F_D\rangle$, using spherical tensor operator techniques (Ver 68a, Ver 69).

The results for the matrix elements of the spin rotation interactions are:

$$<J;F_1,F_2,F_H,F_D|T_{\text{K}}|J;F_1,F_2,F_H,F_D> =$$

$$= \frac{1}{2} J(J+1) \delta(J+1,J-1) \delta(F_1,F_1) \delta(F_2,F_2) \delta(M_H,M_H) \delta(M_D,M_D)$$

$$+ C_{\text{D}(J)} (-1)^J F_1 F_2 F_H F_D \delta(F_1,F_1) \delta(F_2,F_2) \delta(M_H,M_H)$$

$$+ C_{\text{D}(J)} (-1)^J F_1 F_2 F_H F_D \delta(F_1,F_1) \delta(F_2,F_2) \delta(M_H,M_H)$$

$$+ C_{\text{D}(J)} (-1)^J F_1 F_2 F_H F_D \delta(F_1,F_1) \delta(F_2,F_2) \delta(M_H,M_H)$$

$$= \frac{1}{2} J(J+1) \delta(J+1,J-1) \delta(F_1,F_1) \delta(F_2,F_2) \delta(M_H,M_H) \delta(M_D,M_D)$$

$$+ C_{\text{D}(J)} (-1)^J F_1 F_2 F_H F_D \delta(F_1,F_1) \delta(F_2,F_2) \delta(M_H,M_H)$$

$$+ C_{\text{D}(J)} (-1)^J F_1 F_2 F_H F_D \delta(F_1,F_1) \delta(F_2,F_2) \delta(M_H,M_H)$$

$$+ C_{\text{D}(J)} (-1)^J F_1 F_2 F_H F_D \delta(F_1,F_1) \delta(F_2,F_2) \delta(M_H,M_H).$$

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The matrix elements of the quadrupole Hamiltonian are:

$$<J;F_1,F_2,F_H,F_D|Q_{\text{K}}|J;F_1,F_2,F_H,F_D> =$$

$$= \frac{1}{2} J(J+1) \delta(J+1,J-1) \delta(F_1,F_1) \delta(F_2,F_2) \delta(M_H,M_H) \delta(M_D,M_D)$$

$$+ C_{\text{D}(J)} (-1)^J F_1 F_2 F_H F_D \delta(F_1,F_1) \delta(F_2,F_2) \delta(M_H,M_H)$$

$$+ C_{\text{D}(J)} (-1)^J F_1 F_2 F_H F_D \delta(F_1,F_1) \delta(F_2,F_2) \delta(M_H,M_H)$$

$$+ C_{\text{D}(J)} (-1)^J F_1 F_2 F_H F_D \delta(F_1,F_1) \delta(F_2,F_2) \delta(M_H,M_H).$$

To calculate matrix elements of the spin-spin Hamiltonian, it is most convenient to rewrite this operator in terms of scalar products (Ver 64a):

$$<J;F_1,F_2,F_H,F_D|T_{\text{KL}}|J;F_1,F_2,F_H,F_D> =$$

$$= \frac{1}{2} J(J+1) \delta(J+1,J-1) \delta(F_1,F_1) \delta(F_2,F_2) \delta(M_H,M_H) \delta(M_D,M_D)$$

$$+ C_{\text{D}(J)} (-1)^J F_1 F_2 F_H F_D \delta(F_1,F_1) \delta(F_2,F_2) \delta(M_H,M_H)$$

$$+ C_{\text{D}(J)} (-1)^J F_1 F_2 F_H F_D \delta(F_1,F_1) \delta(F_2,F_2) \delta(M_H,M_H)$$

$$+ C_{\text{D}(J)} (-1)^J F_1 F_2 F_H F_D \delta(F_1,F_1) \delta(F_2,F_2) \delta(M_H,M_H).$$

The last matrix element can be evaluated by matrix multiplication. The matrix $(I_0;J)$ is readily obtained from Eq. (3-36) by setting $C_{\text{D}(J)} = 1$. The matrix elements of $(I_0;J)$ are given by:

$$<J;F_1,F_2,F_H,F_D|T_{\text{KL}}|J;F_1,F_2,F_H,F_D> =$$

$$= \frac{1}{2} J(J+1) \delta(J+1,J-1) \delta(F_1,F_1) \delta(F_2,F_2) \delta(M_H,M_H) \delta(M_D,M_D)$$

$$+ C_{\text{D}(J)} (-1)^J F_1 F_2 F_H F_D \delta(F_1,F_1) \delta(F_2,F_2) \delta(M_H,M_H)$$

$$+ C_{\text{D}(J)} (-1)^J F_1 F_2 F_H F_D \delta(F_1,F_1) \delta(F_2,F_2) \delta(M_H,M_H)$$

$$+ C_{\text{D}(J)} (-1)^J F_1 F_2 F_H F_D \delta(F_1,F_1) \delta(F_2,F_2) \delta(M_H,M_H).$$

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removed from the beam. Then the intensity at low exciting field strength is proportional to:

$$|I_{\text{ph}}|^2 = |\langle\psi_2|\psi_1\rangle|^2,$$  \hspace{1cm} (3-39)

where $\psi_2$ is the component of $\mathbf{\Pi}$ along the oscillating electric field.

As the cavity resonates in the $\mathbf{\Pi} \cdot \mathbf{O} \cdot \mathbf{O}$ mode the electric field is oscillating along the axis of the cavity, so $\nu_2 = \nu_3$. By writing the initial $i$ and final state $f$ in terms of the unperturbed initial $\mathbf{g}$ and final $\mathbf{h}$ states, respectively:

$$|i\rangle = E|g\rangle + \epsilon |\mathbf{h}\rangle,$$

$$|f\rangle = E|h\rangle + \epsilon |\mathbf{g}\rangle,$$

the intensity matrix can be written (in matrix notation) as:

$$\mathbf{I} = \mathbf{R}^f \cdot \mathbf{\Pi} \cdot \mathbf{R}^i.$$  \hspace{1cm} (3-37)

Herein

$$C_{ij} = \langle g | u_j | h \rangle,$$  \hspace{1cm} (3-40)

and $R_g$ and $R_h$ are the unitary matrices which diagonalize the Zeeman and hyperfine Hamiltonian of the initial and final state, respectively. In the case of $\mathbf{D}_2\mathbf{O}$ the matrix elements of the intensity matrix $C_{ij}$ is evaluated in the $|J=\mathbf{M}_J \cdot \mathbf{M}_h \cdot \mathbf{M}_l\rangle$ representation:

$$<J:\mathbf{M}_J \cdot \mathbf{M}_h \cdot \mathbf{M}_l| |\nu_1\rangle |J'|:\mathbf{M}_J' \cdot \mathbf{M}_h' \cdot \mathbf{M}_l'\rangle =$$

$$= \frac{1}{2} (-1)^J (-)^{\mathbf{M}_J} (-)^{\mathbf{M}_h} \left( \begin{array}{ccc} J & 1 & J' \\ M & -1 & M' \end{array} \right) \left( \begin{array}{ccc} J & 1 & J' \\ M & 1 & M' \end{array} \right) \delta(M_J, M'_J) \delta(M_h, M'_h).$$  \hspace{1cm} (3-41)

The intensity matrix in case of $\mathbf{D}_2\mathbf{O}$ and $\mathbf{E}_2\mathbf{O}$ is:

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\[ <J=\frac{1}{2}|\sigma J:1:J'|1:J'\sigma>|J,J'\rangle = (3-42) \]

\[ \frac{\hbar}{2} \frac{1}{2} \begin{bmatrix} J-M \hline J-M \end{bmatrix} \begin{bmatrix} J \hline -J \end{bmatrix} \begin{bmatrix} J' \hline J' \end{bmatrix} \delta(J) \delta(J') \delta(M,M'). \]

In the case of HD\(^{17}\)O the energy levels are degenerate with respect to \( M \), as there are no external fields. By summing Eq. (3-40) over the degenerate \( M \) sublevels we find that the hyperfine intensity is proportional to:

\[ |\vec{R}_1 \cdot \vec{E}_1^0|^2. \]

(3-43)

with

\[
\begin{aligned}
& \frac{1}{2} \begin{bmatrix} J+1 \hline J \end{bmatrix} \begin{bmatrix} P_1 \hline P_1 \end{bmatrix} \frac{1}{2} \begin{bmatrix} J+1 \hline 2J+1 \end{bmatrix} \left[ \frac{2J+1}{2J+1} \right] \delta(J+1) \delta(2J+1) \\
\times \left[ \frac{2J+1}{2J+1} \right] \delta(J+1) \delta(2J+1) \\
= (-) \left( \begin{bmatrix} J+1 \hline J \end{bmatrix} \begin{bmatrix} P_1 \hline P_1 \end{bmatrix} \frac{1}{2} \begin{bmatrix} J+1 \hline 2J+1 \end{bmatrix} \delta(J+1) \delta(2J+1) \\
\times \left[ \frac{2J+1}{2J+1} \right] \delta(J+1) \delta(2J+1) \\
\begin{bmatrix} J \hline J \end{bmatrix} \begin{bmatrix} P_1 \hline P_1 \end{bmatrix} \frac{1}{2} \begin{bmatrix} J \hline J \end{bmatrix} \delta(J+1) \delta(2J+1) \\
\end{aligned}
\]

The observed intensities of Zeeman and hyperfine components will generally show deviations from the calculated values, because of the use of high power levels for sensitivity reasons and the action of the state selector (for 55a, 56 a, 57 a, 58 a, 59 a). Noticeable deviations are found in the case of the \( J=2 \rightarrow 2 \) transition of D\(_2\)O (Fig. 1-3) and the \( J=3 \rightarrow 3 \) transition of H\(_2\)O (Fig. 1-6b). Consequently curve-fitting cannot be applied in the analysis of the experimental data.

\section{Experimental Results}

\subsection{Introduction}

This chapter deals with the measurements and analysis of Zeeman and hyperfine splittings of a number of rotational transitions of isotopic species of water. Measurements at zero magnetic field strength, dealing with hyperfine interactions, are described in Sect. 4.3.

In the last section of this chapter the results are discussed of the measurements in an external magnetic field. The method used for the calculation of the coupling constants from the experimental data is given in Sect. 4.2.

\subsection{Calculation of the Zeeman and Hyperfine Coupling Constants from the Experimental Data}

The frequencies of the Zeeman and hyperfine transitions can be expressed in terms of the unperturbed rotational frequency \( v_0 \) and the following coupling constants:

\[ (\alpha_0, \beta_0) \times (\alpha_1, \beta_1, \gamma_1, \delta_1, \epsilon_1, \zeta_1, \epsilon_1' \delta_1', \gamma_1') \]

The first six constants depend on the rotational state \( J \). The Zeeman and hyperfine structure of the \( 2\rightarrow 2 \) transition of H\(_2\)O is, for example, a function of 19 coupling constants apart from the induced Stark effect. Our purpose is to calculate the coupling constants from the experimental data. Unfortunately, some of them cannot be obtained in the present experiments.

The matrix elements of Sect. 3.3 and 3.4 show clearly that the isotropic part of the magnetic susceptibility \( \chi_\text{av} \) cannot be measured. The term containing \( \chi_\text{av} \) gives the same contribution to both \( J \) levels involved in a transition. As a consequence the corresponding contributions cancel in the transition frequencies.

As shown in Sect. 3.7 the nuclear quantum numbers remain unchanged.
<table>
<thead>
<tr>
<th>M</th>
<th>-1</th>
<th>0</th>
<th>1</th>
<th>0</th>
<th>1</th>
<th>0</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>M'</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>g'</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>$a_0$</td>
<td>$-u_B+u_B-18+u_B$</td>
<td>$\sqrt{3}/3$</td>
<td>$2q$</td>
<td>$1/2u_B$</td>
<td>$1/2u_B$</td>
<td>$1/2u_B$</td>
<td>$1/2u_B$</td>
</tr>
<tr>
<td>$b_0$</td>
<td>$1/3u_B$</td>
<td>$1/3u_B$</td>
<td>$1/3u_B$</td>
<td>$1/3u_B$</td>
<td>$1/3u_B$</td>
<td>$1/3u_B$</td>
<td>$1/3u_B$</td>
</tr>
</tbody>
</table>

**Notes:**
1. $u_B$ and $u_B$ are parameters related to the electronic configurations of the molecule.
2. $2q$, $1/2u_B$, and $1/2u_B$ are constants indicating the strength of certain interactions.
3. The table represents the Zeeman and hyperfine submatrix for the J=2 level of HDO, $K_{v}=1$; $u_B=\frac{e}{\hbar}$, $u_B=\frac{e}{\hbar}$, $c_B=\frac{e}{\hbar}$, $Q_e=eq_{e}e_c$, $D_{ij}^{(2)}$, $K_{v}=1$ and $K_{v}=1$.
4. The terms $a_0$, $b_0$, $2q$, $1/2u_B$, and $1/2u_B$ are coefficients that determine the magnetic and hyperfine properties of the molecule.

**Additional Information:**
- The table is used to calculate the magnetic and hyperfine properties of the molecule, which are essential for understanding the behavior of molecules in magnetic fields.
- The parameters $u_B$ and $u_B$ are crucial for determining the strength of the interactions within the molecule.
- The constants $2q$ and $1/2u_B$ help in calculating the magnetic and hyperfine effects accurately.
in an electric dipole transition. The isotropic part of the magnetic shielding will therefore generally cancel in the expression for the transition frequency at high magnetic field strength. The corresponding energy contributions at low magnetic field strength are too small to be measured. The parameter $\xi_2$ cannot be determined accurately for the same reason. The value of $\xi_2$ is therefore taken from other sources and is assumed to be a constant in the present analysis. The following values for the nuclear magnetic moments $\mu_2$ are used (ful 65):

$$\mu_2 = 2.792716 \mu_N,$$

$$\mu_2 = 0.87742 \mu_N.$$  

In addition the coupling constant $\mu_2^{(1)}$ is calculated from the molecular geometry.

In order to calculate the energy splitting of a $J$ rotational level, the Zeeman and hyperfine matrices must be diagonalized. The calculation of the matrix elements, as given in Sect. 3.3 and 3.4, is rather complicated. In addition to the aforementioned large number of parameters appearing in each matrix element, the energy matrices are rather large in the appropriate uncoupled representation. In the case of the $J = 2$ level of HDO we have a 30 x 30 matrix. The matrices can generally be divided in submatrices with the same $\mu_2$ value, because the operator $J_x + I_2 + I_3$ commutes with the Hamiltonian. Furthermore the submatrix for $\mu_2$ can simply be obtained by replacing $I_2$ for $H$ in the submatrix for $\mu_2$. This can be seen both from arguments and from the expressions for the matrix elements. The submatrix $\mu_2 = 2$ of the $J = 2$ level of HDO is shown in Fig. 4.1. To minimize errors all used matrix elements are independently calculated by several persons.

The foregoing shows clearly that the analysis of the experimental data requires a computer. The calculations are carried out on an IBM 360/50 digital computer of the University. The computational method supposes the knowledge of an initial set of approximate values for the coupling constants. These initial values may be known either from previous measurements or from estimates. Starting with these values the perturbation matrices of the initial and the final rotational level are diagonalized. The transition frequencies and relative intensities are calculated from the resulting energy values and the diagonalizing matrices. Transitions with negligible relative intensities are neglected and the remaining transitions are arranged in order of increasing frequencies. The obtained spectrum is compared with the experimental line frequencies. In the next stage the values of the coupling parameters are varied until the best set of values is obtained which reproduces fairly well the experimental line frequencies and intensities. Starting from this set of constants a least squares method is applied in the third stage, yielding the best-fit constants with their errors and corresponding correlation coefficients (Yer 69a).

Measurements at zero magnetic field, dealing only with hyperfine interactions, may be analyzed by setting $B = 0$ in the expression for the matrix elements of the Zeeman and hyperfine Hamiltonian. The accuracy of the values for the hyperfine coupling constants obtained in this way is high enough to use them in the determination of the magnetic coupling constants from Zeeman spectra.

4.3 MEASUREMENTS AT ZERO MAGNETIC FIELD

4.3.1 Hyperfine structure of the $7_1-7_0$ transition of HDO, the $b_3^2 - a_1^2$ transition of D$_2$O, and the $a_3^2 - b_1^2$ transition of H$_2$0

The hyperfine structure of these transitions is investigated in order to check any $J$-dependent centrifugal effects and isotropic effects on the hyperfine tensors at the proton and the deuteron.

A detailed description of the measurements is given elsewhere (Yer 66a, 66b, 67a, 68). The observed hyperfine spectra are interpreted using the hyperfine Hamiltonian of Sect. 3.2.5 by means of the method described in Sect. 4.2. The best-fit values of the coupling constants are given in Table 4.1.

Previous investigations of the centrifugal and isotropic effects involved the coupling constants of the $2_1 - 2_0$ transition of HDO, the $2_2 - 2_0$ transition of D$_2$O, measured by Blyeens et al. (Yer 67), and the $3_2 - 3_0$ transition of H$_2$O, measured in this investigation. The components of the spin-rotation interaction tensor and of the quadrupole interaction tensor were determined and no measurable contributions of
<table>
<thead>
<tr>
<th>Molecule</th>
<th>Transition</th>
<th>Coupling constant</th>
<th>Upper level</th>
<th>Lower level</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDO</td>
<td>2_2^2_1</td>
<td>(eq_1, q_1)^D</td>
<td>86.10(1)</td>
<td>79.16(3)</td>
<td>Blu 67</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C_(B)</td>
<td>-42.36(3)</td>
<td>-41.23(3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>C_(D)</td>
<td>-2.07(1)</td>
<td>-2.04(1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>D_(J)</td>
<td>-2.47</td>
<td>-2.45</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7_1^7_0</td>
<td>(eq_1, q_1)^D</td>
<td>-15.65(20)</td>
<td>-15.65(20)</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C_(B)</td>
<td>-26.15(5)</td>
<td>-26.15(5)</td>
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<tr>
<td></td>
<td></td>
<td>C_(D)</td>
<td>-3.16(3)</td>
<td>-3.16(3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>D_(J)</td>
<td>0.461</td>
<td>0.466</td>
<td></td>
</tr>
<tr>
<td>D_2O</td>
<td>3_2^2_2</td>
<td>(eq_1, q_1)^D</td>
<td>-72.92(2)</td>
<td>49.57(2)</td>
<td>Blu 67</td>
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<tr>
<td></td>
<td></td>
<td>C_(B)</td>
<td>-2.60(1)</td>
<td>-2.60(1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>C_(D)</td>
<td>0.41</td>
<td>-0.46</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4_3^4_1</td>
<td>(eq_1, q_1)^D</td>
<td>78.5(1)</td>
<td>3.3(1)</td>
<td>this work</td>
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<tr>
<td></td>
<td></td>
<td>C_(B)</td>
<td>-2.56(3)</td>
<td>-2.56(3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>C_(D)</td>
<td>-0.84</td>
<td>0.093</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>D_(J)</td>
<td>12.325</td>
<td>9.995</td>
<td></td>
</tr>
</tbody>
</table>

Table 4-1. Experimental hyperfine coupling constants of a number of the rotational levels of HDO, D_2O, and H_2O. All values are in kHz. a) calculated from the molecular geometry.

The centrifugal and isotopic effects could be observed (Blu 67). In spite of this, the indication that these effects can be neglected is open to doubt. In view of the large differences in rotational constants and in the J-values involved, errors due to isotopic effects may be compensated by centrifugal effects.

In order to investigate this possibility the measured hyperfine coupling constants of the 7_1^7_0 transition of HDO and of the 4_3^4_1 transition of D_2O are compared with values calculated from the aforementioned components of the relevant tensors. Analysis indicates (Ver 68) that the rigid rotor approximation is good within the experimental error for the deuteron spin-rotation constant C_(J). Agreement for the C_(D) and (eq_1, q_1)^D constants is not better than within 2–5 times the experimental error.

The present investigation shows that within the accuracy of the present experiments, centrifugal and isotopic effects have measurable contributions. For further investigation of these effects it is desirable to obtain more experimental values of the hyperfine coupling constants.

### 4.3.2 Hyperfine structure of HD^{17}O

The measurements are performed on an enriched sample of HD^{17}O prepared at the Oak Ridge National Laboratory. The ^17O enrichment of the sample (0.8 g) is 9.5 %. This amount is sufficient for a run of about 40 minutes at an effusion pressure of 1 Torr. A freezing-recovery procedure is applied in order to get a total measuring time of a few hours. However the sample got quite heavily contaminated after a number of runs and freezing-recovery operations. In addition, experiments or transitions of HD^{15}O and D_2O with a similar Stark effect showed a preferential state selection causing a weakening of the transitions lying in the lower frequency range of the spectrum. For these reasons we have measured only the high frequency range of the spectrum.

In the first run the high-frequency part of the spectrum is scanned at a rather high sweep rate in order to get the position of the groups of lines. In the subsequent runs each group is recorded at a low sweep rate yielding accurate frequencies of the individual hyperfine transitions. The measured frequencies and their errors are listed in Table 4-2. Figure 4-2 shows a recording of a group of hyperfine transitions. A large fraction of the experimental errors of the line frequencies originates in the uncertainty in the determination of the top of the lines distorted by dispersion effects. The signal to noise ratio varies from 2 to about 40.
Table 4.2. The calculated relative intensities $I_{\text{calc}}^{\text{rel}}$ and the measured and calculated line positions $v_{\text{meas}}$ and $v_{\text{calc}}$, respectively, of the high-frequency hyperfine spectrum of the $2_2^{-1}$ rotational transition of HDT. All frequencies are given in kilohertz relative to the central line. The relative intensities are calculated for the case of conventional microwave spectroscopy.

As shown in Sec 3.6 the hyperfine splittings and line frequencies are determined by 16 (eight for each level) coupling constants:

\[
\{n_{\text{J}_1}, q_{\text{J}_1}, q_{\text{J}_2}, q_{\text{J}_3}, q_{\text{J}_4}, q_{\text{J}_5}, q_{\text{J}_6}, q_{\text{J}_7}, q_{\text{J}_8}, q_{\text{J}_9}, q_{\text{J}_{10}}, q_{\text{J}_{11}}, q_{\text{J}_{12}}, q_{\text{J}_{13}}, q_{\text{J}_{14}}, q_{\text{J}_{15}}, q_{\text{J}_{16}}\}
\]

Values of the spin-spin coupling constants $B_{\text{J}_1}^{\text{HD}}$, $B_{\text{J}_1}^{\text{OH}}$, and $B_{\text{J}_1}^{\text{OD}}$ are calculated from Table 3.2 using known geometrical parameters and the values of $J_{\text{f}}$. The average values of $J_{\text{f}}$ and the principal axes and moments of inertia are calculated by assuming for HDT the same geometry as for HDT.

In this way the number of coupling constants to be deduced from the observed spectra is reduced to 10. But even with this number of constants only poor accuracy can be expected for the hydrogen and deuterons constants $C_{\text{J}_1}$, $C_{\text{J}_1}$, and $q_{\text{J}_1}$, if they are handled as adjustable parameters to fit the spectrum. The corresponding interactions give rise to splittings only within each group of lines.

Fig. 4.2. A recording of a group of hyperfine transitions of HDT.
which for HD\textsuperscript{17}O can be determined only with considerably larger errors than for HD\textsuperscript{16}O and D\textsubscript{2}O. It has been shown in Sect.4.3.1 that the dependence of coupling constants at the hydrogen and deuterium nuclei in HD\textsubscript{0}, D\textsubscript{2}O, and H\textsubscript{2}O upon rotational state and isotopic substitution is in a rather good agreement with theory based on the rigid rotor approximation. Assuming that this theory is (evidently) valid also for HD\textsuperscript{17}O the six constants: \(C_{11}, C_{12}, C_{21}, C_{22}, (eq_{2}q_{1}(D))\) and \((eq_{2}q_{1}(D))\) of HD\textsuperscript{17}O can be obtained from the corresponding constants of HD\textsuperscript{16}O by a sequence of scale-, rotation-, and reflection transformations (Ver 688). This procedure is applied to obtain the proton and deuterium constants shown in Table 4-3. Effects of possible errors in these constants, because of the deviations quoted in Sect.4.3.1, can be neglected in view of the experimental errors in the transition frequencies (Table 4-2). The remaining four coupling constants \((eq_{2}q_{1}(D)), (eq_{2}q_{1}(D))_{21}, C_{22}, \) and \(C_{22}\) are obtained from the fit of experimental and theoretical spectra using the IBM 360/50 computer.

The best fit hyperfine constants are listed in Table 4-3. The hyperfine spectrum calculated with these constants is given in Table 4-2, together with the experimental values. Agreement between calculated and observed relative intensities is generally good.

### 4.4 THE ZEEMAN EFFECT

#### 4.4.1 Performance

The first order Zeeman effect is by far the largest interaction causing splittings of the order of 5 MHz at magnetic fields of the order of 10 kG. As shown in Sect.3.3 and 3.4 this splitting is given by the expression:

\[
\Delta \nu_{J=\pm 1} = -\left(\mathbf{g}_{J} \cdot \mathbf{\mu}_{B}\right) B.
\]

The frequencies of the transitions, obeying the selection rule \(M_{J} = \pm 1\), are given by:

\[
n \nu = \nu_{0} \pm \left(\mathbf{g}_{J} \cdot \mathbf{\mu}_{B}\right) B = \left(\mathbf{g}_{J} \cdot \mathbf{\mu}_{B}\right) B,
\]

where \(\nu_{0}\) is the transition frequency in the absence of both external fields and hyperfine interactions, and \(\mathbf{g}_{J}\) and \(\mathbf{\mu}_{B}\) represent the rotational molecular magnetic moments of the higher and the lower level, respectively, of the transition in question.

It is seen from Table 4-1 that the \(\mathbf{g}_{J}\) and \(\mathbf{g}_{J}\), involved in a specific transition are nearly equal. Consequently the spectrum consists of two groups of lines, centered at \(\nu_{0} \pm \left(\mathbf{g}_{J} \cdot \mathbf{\mu}_{B}\right) B\) and extending over about \(2\left(\mathbf{g}_{J} \cdot \mathbf{\mu}_{B}\right) B\).

Each line within such a group is split because of hyperfine interactions. In case of HDO at 12 kG these groups of lines are
situated at a distance of ± 5 MHz from the unsplit line and contain lines distributed over a region of about 0.5 MHz.

It would take several hours to measure both groups of lines in one experimental run. Apart from difficulties to keep the magnetic field well stable over such a long time, only a few spectra a day can be obtained. For these reasons a different procedure is followed.

After the magnetic field is stabilized, one group of lines is measured a number of times. At another time the other group of lines is measured thoroughly. The relation between the magnetic field in the cavity and at the point of calibration may change between these two sets of measurements because of cycling and temperature effects. To correct for this change two single lines, one of each group, are measured accurately in both series of measurements. Their frequencies obtained in the first series are compared with the frequencies obtained in the second series of experiments. In this way the change of the magnetic field in the cavity between the two series is determined.

The magnetic coupling constants are calculated from the frequencies of the single lines appearing in the Zeeman spectrum by means of the least squares method described in Sect.4.2.

The value of the unsplit line position \( \nu_0 \) is determined either from the experimental data by introducing \( \nu_0 \) as a parameter in the least squares fit, or from the measured position of a specific single line of the hyperfine spectrum at zero magnetic field. If the hyperfine coupling constants are known, the value of \( \nu_0 \) follows from the position of this single line. An adequate fit these two values must agree.

The Zeeman experiments are performed with cavities 16 cm long, giving a half width of about 1.8 kHz. Vapour pressures of about 0.1 Torr are used in the source chamber. Apart from the \( \text{H}_2\text{O} \) transition, the spectra are measured with a time constant of 1 sec of the lock-in amplifier. The \( \text{H}_2\text{O} \) transition is measured by means of the CNT.

4.4.2 Zeeman effect of the \( ^2 \Sigma_\text{g} \rightarrow ^2 \Sigma_\text{u} \) transition of \( \text{H}_2\text{O} \)

In the first set of experiments the splittings are measured in a magnetic field of 5 kG. The theoretical line positions are brought into a rough agreement with the measured frequencies by varying slightly the initial values of the molecular magnetic moments of the \( ^2 \Sigma_\text{g} \) and \( ^2 \Sigma_\text{u} \) levels of \( \text{H}_2\text{O} \) listed in Table 4.1. Starting from these values, a least squares fit yields the best-fit values of the molecular magnetic moments at 5 kG:

\[
\begin{align*}
\mu_0^- &= 0.54751 \quad (26) , \\
\mu_0^+ &= 0.54945 \quad (26) .
\end{align*}
\]  

(4.1)

Second order magnetic effects are not important at this field strength and are neglected. The linear Zeeman effect is then calculated for several values of the magnetic field strength using the \( \mu_0^+ \)'s of Eq. (4.1). These calculations show that a sufficient number of isolated transitions can be expected at 12 kG to determine the contribution of magnetic susceptibility to the molecular energy.

At 12.009 kG both groups of transitions, with signal to noise ratios from 5 to 80, are measured six times to determine the frequencies of the isolated lines. Figure 2-6 shows the Zeeman effect of the \( ^2 \Sigma_\text{g} \rightarrow ^2 \Sigma_\text{u} \) transition of \( \text{H}_2\text{O} \). The experimental frequencies of the isolated transitions are given in Table 4.5.

It is shown in Sect.3.5 that the induced Stark effect at a magnetic field of 12 kG cannot be neglected. This effect gives energy splittings \( \Delta \nu'_{1M} \), which can be written as:

\[
\Delta \nu'_{1M} = (A_{1J} + B_{1J} M_J^0)^2 B^2 ,
\]  

(4.2)

where \( \nu \) is assumed to be perpendicular to the direction of the magnetic field. This velocity is not uniform in the molecular beam.

Assuming a molecular velocity distribution as given by Ramsey (Ann 56, p 20) and neglecting the dependence of the transition probability on the molecular velocity, expression (4.2) may be written as:

\[
\Delta \nu'_{1M} = (A_{1J} + B_{1J} M_J^0)^2 \nu^2 B^2 ,
\]  

(4.3)

where \( a \) is the most probable velocity. At room temperature this splitting is about 200 Hz.
<table>
<thead>
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<th>$^2\Delta_g-^2\Pi_g$</th>
<th>$^2\Delta_g-^2\Pi_g$</th>
<th>$^2\Delta_g-^2\Pi_g$</th>
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<tr>
<td></td>
<td>Bur 53</td>
<td>Bur 53</td>
<td>Bur 53</td>
<td>Bur 53</td>
</tr>
<tr>
<td>g(up)</td>
<td>0.9480(22)</td>
<td>0.551(6)</td>
<td>0.33178(13)</td>
<td>0.338(10)</td>
</tr>
<tr>
<td>g(low)</td>
<td>0.94980(22)</td>
<td>0.551(6)</td>
<td>0.3334(13)</td>
<td>0.357(10)</td>
</tr>
<tr>
<td>g(up)/g(low)</td>
<td>0.9997(18)</td>
<td>0.995078(16)</td>
<td>0.96310(10)</td>
<td>0.96310(10)</td>
</tr>
<tr>
<td>$\chi_L(\text{up})$</td>
<td>17.3(15)</td>
<td>17.5(37)</td>
<td>27.4(96)</td>
<td>27.4(96)</td>
</tr>
<tr>
<td>$\chi_L(\text{low})$</td>
<td>18.3(15)</td>
<td>17.5(39)</td>
<td>-2.4(133)</td>
<td>-2.4(133)</td>
</tr>
<tr>
<td>$\delta(x_1; x_2; x_3; x_4; x_5; x_6)$</td>
<td>-0.461</td>
<td>0.93</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>$\delta(H_1; H_2; H_3; H_4; H_5; H_6)$</td>
<td>0(4) x 10^{-6}</td>
<td>0(4) x 10^{-6}</td>
<td>0(4) x 10^{-6}</td>
<td>0(4) x 10^{-6}</td>
</tr>
<tr>
<td>$\delta(D_1; D_2; D_3; D_4; D_5; D_6)$</td>
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<td>-1.2(30) x 10^{-6}</td>
<td>-12(43) x 10^{-6}</td>
<td>-23(42) x 10^{-6}</td>
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<tr>
<td>$\delta(x_1; x_2; x_3; x_4; x_5; x_6)$</td>
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<td>0(47) x 10^{-6}</td>
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<td>0.96</td>
</tr>
<tr>
<td>$\delta(x_1; x_2; x_3; x_4; x_5; x_6)$</td>
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<tr>
<td>$\delta(x_1; x_2; x_3; x_4; x_5; x_6)$</td>
<td>0(278.825.89(4))</td>
<td>0.99420(1.1)</td>
<td>10947133.4(1)</td>
<td>10947133.3(15)</td>
</tr>
<tr>
<td>$\nu_0 = 0$</td>
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<td>10919420.1(1)</td>
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<td>10947133.3(15)</td>
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</table>

Table 4-4. Measured values of the magnetic coupling constants and of the unsplit line position of the molecules HDO, D$_2$O, and H$_2$O. The upper level involved in the transition is indicated as "up" and the lower level as "low". The constants $\chi_L$ are given in $10^{-7}$ kHz $\Delta_g$, the parameter $\nu_0$ in kHz, and the remaining quantities are dimensionless.

Table 4-5. Measured and calculated values of the $^2\Delta_g-^2\Pi_g$ transition of HDO at 12.8 GHz.

The frequencies are given in kHz with respect to $\nu_0$ = 5078.969 MHz.
However, the velocity distribution in the beam will generally deviate from the distribution assumed in the derivation of expression (4-2) because of the action of the state selector which may result in velocity selection. If these effects are taken into account, the correction for the Stark splitting has an uncertainty of about 80 Hz. This uncertainty together with the experimental error of the line positions yields an overall error of 150 Hz.

The parameters $e_\perp$, $e_\parallel$, $g_\perp$, $g_\parallel$ and their error matrix are calculated with the aid of the least squares method from the isolated frequencies in the Zeeman spectrum. The interaction parameter $e_\perp$ gives splittings which are approximately three times smaller than those of the $e_\parallel$ interaction. The constant $c_\parallel$ is therefore neglected in the analysis of data (Table 4-4).

The magnetic field strength is assumed to be a constant in the above analysis. Figure 2-1 shows that the magnetic field strength can be assumed to be known within about 0.04 %. With this uncertainty in the magnetic field, the error matrix of the couplings constant is calculated by means of the expressions for the propagation of errors (Ver 69a).

The final results for the coupling constants and $\nu_0\gamma$ are listed in Table 4-4. This table shows that the values of the best-fit unsplit line position agrees with the value measured at zero field, and that the values for magnetic moments agrees with the values obtained at 5 kOe (Eq. 4-1). The Zeeman and hyperfine transition frequencies are calculated from the magnetic and hyperfine coupling constants, the unsplit line position, and the Stark contribution. Comparison of the calculated frequencies of the isolated transitions (given in Table 4-5), with the measured values shows a good fit.

### Table 4-6

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<th>Calculated frequency</th>
<th>Measured relative intensity</th>
<th>Calculated frequency</th>
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</table>

4.1.3 Zeeman effect of the 3-2 and the 3-1 transition of $D_{2,0}$

The signal to noise ratio of the Zeeman components of the 3-2 $D_{2,0}$ transition varies from 2 to 50. Several of the Zeeman components are not resolved. For an accurate determination of the frequencies of isolated transitions in the spectrum, both groups of lines are measured 12 times. The resulting values of the transition frequencies at 1209 kOe. The frequencies are given in kHz relative to $\nu=10,919.420.0$ kHz. The relative intensities are calculated for the case of conventional microwave spectroscopy.
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Table 4-7. Measured and calculated values of the Zeeman and hyperfine transition frequencies of the $4_s-5_s$ transition of D$_2$O at 12009 Ks. The frequencies are given in K$s$ relative to $\nu$=10,947,117.0 K$s$. The relative intensities are calculated for the case of conventional microwave absorption spectroscopy.
12.009 kg are given in Table 4-6. Figure 4-3 shows a typical example of the Zeeman and hyperfine structure of this transition at 12.009 kg.

As discussed in Sect. 2.5.1, the Zeeman components of the 6_{3}^{+}5_{1} transition of H_2\_O have substantially lower intensities than those of the 3_{1}^{+}2_{0} transition. The measured signal-to-noise ratio is not greater than about eight, and the spectra show a large number of isolated transitions. Each group of lines is measured seven times. The resulting values for the transition frequencies at 12.009 kg are listed in Table 4-7. Figure 4-3 shows the recorded Zeeman and hyperfine spectrum at 12.009 kg. More detailed information is given elsewhere (Ver 68a).

The experimental data are analyzed by the least squares method as described in Sect. 4.2. The induced Stark effect can be neglected in the analysis of these transitions. The final results for the coupling constants, including the uncertainty in the magnetic field strength, are listed in Table 4-4. This table shows that the best-fit unsplit line positions ν₀ agree with the zero field values. Finally the frequencies of all Zeeman and hyperfine transitions are calculated from the set of Zeeman and hyperfine coupling constants and ν₀. The calculated values for the isolated transitions, given in Tables 4-6 and 4-7, are in good agreement with the experimental frequencies.

### 4.4 Zeeman effect of the 6_{3}^{+}5_{1} transition of H_2O

Preliminary calculations show that the Zeeman spectrum of this transition of H_2O consists of a number of isolated frequencies. As discussed in Sect. 2.5.1 the very low maser intensities of Zeeman components require the application of time averaging techniques. Sampling the spectra in the CAT over a period of one hour at a sweep rate of 3.5 kHz per sec, a signal to noise ratio of about three can be achieved. Consequently only the Zeeman transitions of high relative intensity can be measured within a reasonable time. It is clear that contributions of the magnetic shielding and susceptibility cannot be measured because of the low resolving power at this signal to noise ratio. Another difficulty comes from the determination of the magnetic field strength in the cavity. Because of the smallness

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Table 4-8. Measured and calculated values of the Zeeman and hyperfine transition frequencies of the 6_{3}^{+}5_{1} transition of H_2O at 10005 kg. All frequencies are given in kHz relative to the unsplit line position: ν₀ = 292,235,079,460 kHz. The relative intensities are calculated for the case of conventional microwave absorption spectroscopy.
of the cavity (diameter 1.05 cm) it is impossible to measure the field inside the cavity with the NMR probe (diameter 1.9 cm). To eliminate this difficulty, the relation between the field at the calibration point and in the cavity is assumed to be the same as for the HO cavity. There is a number of indications that this assumption is essentially correct. No change in the magnetic field strength at the central point is observed with the cavity as closely as possible to the probe and without the cavity. Furthermore, the relation between the field at the calibration point and in cavities with larger cavity diameters turns out to be independent on the specific cavity. The resulting frequencies of 14 Zeeman transitions at 10.005 kG are listed in Table 4-8. A least squares fit yields the molecular magnetic moments for the levels involved in the transition. The values are listed in Table 4-4. The frequencies of the Zeeman and hyperfine transitions at 10.005 kG are calculated from the coupling constants. These values, listed in Table 4-8, show a good agreement with experimental frequencies.

Fig. 4-4. A recording of a part of the Zeeman and hyperfine spectrum of the 6.5-5.4 transition of H$_2$O. Distance between frequency markers is 3 kHz.

CHAPTER 5

INTERPRETATION AND DISCUSSION OF THE RESULTS

5.1 INTRODUCTION

Recently calculations of one-electron properties for the ground state of water have been performed by several authors, using various choices of the LCAO-MO-SCF wave functions (Kar 67, Am 68, Neu 68). In order to test the accuracy of the resulting charge distributions, the values of several one-electron properties obtained from the present experiments are compared in this chapter with the theoretical results.

The components of the quadrupole coupling tensor at the oxygen nucleus are discussed in Sect.5.2. Our results agree quite well with theoretical calculations, but they differ significantly from the experimental results of Stevenson and Townes (Ste 57).

The molecular magnetic moments are analysed and discussed in Sect.5.3. The paramagnetic electronic contributions to the tensor elements are evaluated. Simplified theories of Pople (Pcp 62) and of Karpplus and Das (Kar 60) fail to explain these experimental quantities as shown in Sect.5.3.2.

It is interesting to investigate the question if a relationship can be obtained between the molecular g-values and the spin-rotation coupling constants by treating $r^{-3}$ parametrically in the spin-rotation tensor. The complete data on the diagonal elements of these tensors obtained in this work make it possible to test such a relationship. It is felt that this approach to the electron-coupled spin-rotation interaction constants is more meaningful than the attempt to reduce the second order term to an expression which depends only on electronic ground state and an average excitation energy (Sai 54). The failure of an analogous reduction for the paramagnetic molecular moments is well known (Sect.5.3.2).

The relationship between the molecular magnetic moments of isotopic species of water and the molecular electric dipole moment is investigated in Sect.5.3.4. A substantial dependence of the elements
of the molecular magnetic tensor of the isotopic species on the vibrational state is found.

Section 5.4 deals with the molecular magnetic susceptibility tensor. Only anisotropies in the diagonal elements can be obtained from the experimental results. The paramagnetic susceptibility is calculated from the molecular magnetic moments. The remaining anisotropies in the diamagnetic part, which depend only on the ground state wave function, are compared with calculated values in Sect. 5.6. As shown by Ramsey (Ref. 50), the anisotropies in the magnetic susceptibility and the rotational magnetic moment tensors can be related to the molecular quadrupole moment.

As the principal axes of the molecular quadrupole moment and inertial tensors coincide in case of D_2O, the entire quadrupole moment tensor is obtained for this molecule (Sec. 5.4.3). The individual elements of the magnetic susceptibility tensor are obtained by combining (Sect. 5.4.3) the anisotropies in the tensor elements with the average magnetic susceptibility obtained by conventional methods (Ref. 56).

The isotopic dependence in the elements of the magnetic susceptibility tensor is discussed in Sect. 5.4.4.

Section 5.5 deals with the measured isotropies in the magnetic shielding of the deuteron and the proton.

Comparison of the computed one-electron properties, which depend only upon the wave function of the molecular ground state, with the results of the present experiments is the subject of Sect. 5.6.

5.2 THE HYPERFINE TENSORS OF THE OXYGEN NUCLEUS IN HD^{17}O

The diagonal elements of the electric quadrupole coupling tensor at the oxygen nucleus of HD^{17}O in the (a, b, c) coordinate system are obtained from the two measured values of \( \langle q^2 \rangle \), using the expressions for the quadrupole coupling constant, listed in Table 5.2, and the Laplace's equation. The required values of \( \langle q^2 \rangle \) are calculated assuming the nuclear geometry of HD^{17}O as given in Fig. 5-1.

It follows from symmetry considerations that the quadrupole coupling tensor at the oxygen nucleus is diagonal in the (x, y, z) coordinate system (Fig. 5-1), if we assume validity of the rigid rotor model.
and isotopic invariance of the charge distribution. The diagonal elements in this coordinate system are obtained from the measured coupling constants by rotating the \((a, b, c)\) axes to the \((x, y, z)\) axes. The off-diagonal tensor component \(\langle \text{eq} \frac{2}{3} x^2 y^2 \rangle (0)\) is determined by rotating the \((x, y, z)\) axes back to the \((a, b, c)\) axes. The resulting values for the non-zero components of the quadrupole coupling tensor are in kHz:

\[
\begin{align*}
\langle \text{eq} \frac{2}{3} x^2 y^2 \rangle (0) &= -7878(8) \\
\langle \text{eq} \frac{2}{3} x^2 y^2 \rangle (0) &= -2297(72) \\
\langle \text{eq} \frac{2}{3} x^2 y^2 \rangle (0) &= 10175(67) \\
\langle \text{eq} \frac{2}{3} x^2 y^2 \rangle (c) &= -2985(31)
\end{align*}
\]

The asymmetry parameter \(\eta\) is defined as:

\[
\eta = \frac{\langle \text{eq} \frac{2}{3} x^2 y^2 \rangle (0)}{\langle \text{eq} \frac{2}{3} x^2 y^2 \rangle (0)}.
\]  
(5-2)

In the case of \(\text{HD}^{17}O\) we get from our results; \(\eta = 0.75(1)\). This result differs considerably from the value determined by Stevenson and Townes \((\eta = 1.83(20))\), but it is in good agreement with recent ab-initio calculations as discussed in Sect. 5.6.

It is not possible to obtain the components of the quadrupole coupling tensor at the oxygen nucleus because only two equations, one for each level, are available for the three diagonal elements \(\tilde{\eta}_{xy}^{(0)}\).

5.2 THE MOLECULAR MAGNETIC TENSOR

5.3.1 The tensor elements of \(\text{D}_2O\)

The expression for the molecular magnetic moment in terms of the diagonal elements \(\tilde{\eta}_{ii}\), where \(\tilde{\eta} = \tilde{\eta}^{(0)} + \tilde{\eta}^{(a)}\), is given in Table 3-2. The required values of \(\langle \delta^2 \rangle\), listed in Table 3-2, are obtained from the molecular rotational constants also given in Table 5-1.

A least squares fit of the four measured molecular magnetic moments \(\tilde{\eta}_{x}^{(0)}, \tilde{\eta}_{y}^{(0)}, \tilde{\eta}_{z}^{(0)}\) and \(\tilde{\eta}_{x}^{(a)}\) of \(\text{D}_2O\) yields for the diagonal elements of the \(\tilde{\eta}\) tensor:
\[
G_{\text{aa}} = 0.32530(10),
\]
\[
G_{\text{bb}} = 0.36009(22),
\]
\[
G_{\text{cc}} = 0.32513(15).
\]

The off-diagonal elements are zero because of the \(C_{2v}\) symmetry of \(D_2O\).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Rotational state</th>
<th>Experimental g-values</th>
<th>Calculated g-values</th>
</tr>
</thead>
<tbody>
<tr>
<td>(D_2O)</td>
<td>(3)</td>
<td>0.3310 (13)</td>
<td>0.3310</td>
</tr>
<tr>
<td>(D_2)</td>
<td>(2)</td>
<td>0.3330 (13)</td>
<td>0.3330</td>
</tr>
<tr>
<td>(H_2)</td>
<td>(4)</td>
<td>0.3290 (13)</td>
<td>0.3290</td>
</tr>
<tr>
<td>(F)</td>
<td>(5)</td>
<td>0.3415 (13)</td>
<td>0.3415</td>
</tr>
</tbody>
</table>

Table 5-3. Measured and calculated values for some rotational magnetic moments of \(D_2O\).

From the very good fit of the \(G_{\text{ab}}\) values (Table 5-3) of the four \(J\) levels, we may conclude that centrifugal distortion has apparently no measurable influence on the \(G_{\text{ab}}\) values for \(D_2O\) up to \(J = 5\). This may be caused by the cancellation of the centrifugal corrections to the nuclear part \(g^{(n)}\) and the electronic part \(g^{(e)}\). To show this let us consider the nuclear part.

Substituting the expression for \(A_{\text{g}}\) into the expression for \(g^{(n)}_{\text{gg}}\) (Table 5-1) we get:

\[
g^{(n)}_{\text{gg}} = \frac{\mu_{\text{g}}}{\mu_{\text{g}} + \mu_{\text{s}}} \frac{5}{K} \frac{\mu_{\text{g}}}{\mu_{\text{g}}} \frac{(2J+1)}{L} \frac{(J^2 - L^2)}{J^2},
\]

(5-4)

If the ratio \(\mu_{\text{g}}/\mu_{\text{g}}\) is a constant independent of \(K\), \(g^{(n)}_{\text{gg}}\) is independent of nuclear positions. This is almost the case for \(D_2O\). By substituting the values for the nuclear masses, Eq. (5-4) can be written as (Ref 69a):

\[
g^{(n)}_{\text{gg}} = 0.3500 - \frac{0.04171 \frac{J^2}{L^2}}{16 \pi^2 \alpha^2 (\frac{L}{\alpha})^2 + 4.0942 \frac{L^2}{D^2}}.
\]

(5-5)

The \(r\)-dependent part of the term in square brackets represents only a slight correction (about 1%) on the first (constant) part. Centrifugal distortion affects only the last part. This effect is estimated from the results obtained by Posener and Strandberg (Ref 54) to be less than 1% of the \(r\)-dependent term for the levels of \(D_2O\) involved in this work. Consequently the one of \(g^{(n)}_{\text{gg}}\) will be constant to within \(10^{-4}\) under centrifugal distortion.

The influence of this effect on \(g^{(e)}_{\text{gg}}\) can be estimated using the relation:

\[
g^{(e)}_{\text{gg}} = g^{(e)}_{\text{gg}} - g^{(n)}_{\text{gg}}.
\]

where \(g^{(e)}_{\text{gg}}\), \(g^{(n)}_{\text{gg}}\), and \(g^{(n)}_{\text{gg}}\) are roughly of the same magnitude. As can be seen from Eq. (5-3) the elements \(g^{(e)}_{\text{gg}}\) are independent of \(J\) and within \(10^{-7}\). Consequently the influence of the centrifugal distortion on \(g^{(e)}_{\text{gg}}\) will be less than \(10^{-7}\).

Using Eq. (5-5), the values of \(g^{(n)}_{\text{gg}}\) are calculated from the molecular geometry given in Fig. 5-1. The results are:

\[
g^{(n)}_{\text{aa}} = 0.5008,
\]
\[
g^{(n)}_{\text{bb}} = 0.5004,
\]
\[
g^{(n)}_{\text{cc}} = 0.5006.
\]

(5-6)

Comparison of these values with the values of Eq. (5-3) yields the electronic contribution to \(G\):

\[
g^{(e)}_{\text{aa}} = -0.1755(1),
\]
\[
g^{(e)}_{\text{bb}} = -0.1403(2),
\]
\[
g^{(e)}_{\text{cc}} = -0.1755(2).
\]

(5-7)
5.3.2 Determination and discussion of the quantity

$$I_{y_0} = \left( L_s - L_n \right)^{-1}\left\langle \psi \left| L_x \right\rangle \right| \right| L_x \left\rangle \right| \right|^2$$

From the definition of $\Omega_{86}$ one can easily derive a relation between the electronic part $\Omega_{86}(e)$ of the magnetic tensor and

$$\sum_{n=0}^{y_0} \left( L_s - L_n \right)^{-1}\left\langle \psi \left| L_x \right\rangle \right| \right| L_x \left\rangle \right| \right|^2 = \frac{\Omega_{86}(e)}{\Omega_{86}(e)} \right| \right| L_x \left\rangle \right| \right|^2.

(5-8)

where $L_x$ is defined with respect to the center of mass of $D_2O$. In the following, the quantity $\sum_{n=0}^{y_0} \left( L_s - L_n \right)^{-1}\left\langle \psi \left| L_x \right\rangle \right| \right| L_x \left\rangle \right| \right|^2$ is often abbreviated as $I(L_s, L_x)$.

Substitution of the values of $\Omega_{86}(e)$ of Eq.(5-7) yields values for the quantity $I(L_s, L_x)$. The results are given in Table 5-4.

<table>
<thead>
<tr>
<th>Center of mass</th>
<th>Deuteron nucleus (a)</th>
<th>Oxygen nucleus (a)</th>
<th>Oxygen nucleus (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I(L_s, L_x)$</td>
<td>$-0.1089(1)$</td>
<td>$-1.251(1)$</td>
<td>$-0.2876(3)$</td>
</tr>
<tr>
<td>$I(L_s, L_x)^b$</td>
<td>$-0.147(2)$</td>
<td>$-1.385(1)$</td>
<td>$-0.30$</td>
</tr>
<tr>
<td>$I(L_s, L_x)^c$</td>
<td>$-0.2760(3)$</td>
<td>$-2.076(3)$</td>
<td>$-0.78$</td>
</tr>
</tbody>
</table>

Table 5-4. Values of $I(L_s, L_x)$ at several points in the $D_2O$ molecule. All values are in $10^{-5}$ kg m$^{-2}$.

a) Calculated from the electronic contribution to the molecular magnetic moment.

b) Calculated from the molecular electronic wave function of Ellison and Shull (Ell 55).

The quantity $I(L_s, L_x)$ can be transformed to any point $P$ in the molecule with the aid of the relation (Lo 66, Neu 68):

$$I(L_s, L_x) = \frac{I(L_{s_x}, L_{x})}{L_{y_0}} + \sum_{a}(\frac{I(L_{a}, L_{x})}{L_{y_0}}) + \sum_{b}(\frac{I(L_{b}, L_{x})}{L_{y_0}}).$$

(5-9)

where $\text{G}$ represents the position vector of $P$ in the center of mass system of $D_2O$, $L_{y_0}$ is the position vector of $0$-th electron with respect to $CM$, and $L_{y_0}$ is the $g$-th component of the electronic angular momentum with respect to $P$. The quantities $I(L_{a}, L_{x})$ and $I(L_{b}, L_{x})$ are calculated from the molecular electronic dipole moment, which is directed along the $b$-axis: $\nu = 1.65 \, \text{D}$.

The quantity $I(L_s, L_x)$ is calculated both with respect to the oxygen and to the deuteron nucleus. The results are given also in Table 5-4.

For the analysis of these values, let us first assume a very simple model for the electronic distribution, consisting of the closed inner shells electrons at the oxygen nucleus and two pairs of $\pi$ valence electrons. The inner shell electrons feel an almost spherical symmetry and will slip almost completely, thus contributing very little to $I(L_s, L_x)$. Each pair of $\pi$ bond electrons feels an almost cylindrical symmetry about their bond line. For each pair considered individually, the contribution to $I(L_s, L_x)$ with $g$ along the bond line will be zero, whereas it will be equal along the two axes at right angles to this line. One can thus write for each bar in the $g$-axes system:

$$I(L_{s_x}, L_{x}) + I(L_{a_x}, L_{x}) = I(L_{b_x}, L_{x}).$$

(5-10)

Neglecting overlap effects of the two bars Eq.(5-10) will also hold for the molecular values. Table 5-4 shows that this statement holds within about 20%.

We shall now try to analyze the values of $I(L_s, L_x)$ on the basis of LCAO-MO theory (See Sect. 5.6.1). Within the single determinant approximation, the many electron molecular orbital wave function $\psi$ of a molecule, with total electron spin equal to zero, is a Slater determinant constructed of molecular orbitals (MO) $\psi_a$ and electron spin orbitals $\alpha$ and $\beta$. 97
In the LCAO-MO theory the MO's are further approximated by linear combinations of atomic orbitals \( \psi \) centered at the various points in the molecule:

\[ \psi_\alpha^\alpha = \sum \psi_\alpha \psi_\beta \]

(5-11)

Using LCAO-MO self consistent field equations, the resultant number of electronic energy levels is equal to the number of AO's included in the basis set. In the molecular ground state, the lower energy levels are filled with the electrons leading to a number of unoccupied energy levels. Generally, the \( ^1 \Sigma \) molecular electronic ground state can be written as:

\[ \psi_0 = \frac{1}{\sqrt{C_0}} \left| \psi_1(1) \psi_2(2) \psi_3(3) \psi_4(4) \ldots \ldots \right| \]

\[ \psi_p = \frac{1}{\sqrt{C_p}} \left| \psi_1(1) \psi_2(2) \psi_3(3) \psi_4(4) \ldots \ldots \right| \]

(5-12)

where \( 2n \) is the number of electrons and \( \psi_n \) through \( \psi_n \) are the \( n \) MO's with lowest orbital energies. In this model the excited molecular electronic states (with total electron spin equal to zero) are then obtained from expression (5-12) by replacing one or more of the \( \psi_i \) 's by \( \psi_p \) 's, where \( \psi_p \) are unoccupied MO's in the molecular ground state. For example:

\[ \psi_i = \frac{1}{\sqrt{C_i}} \left| \psi_1(1) \psi_2(2) \psi_3(3) \psi_4(4) \ldots \ldots \right| \]

\[ \psi_p = \frac{1}{\sqrt{C_p}} \left| \psi_1(1) \psi_2(2) \psi_3(3) \psi_4(4) \ldots \ldots \right| \]

(5-13)

with \( \psi_p \) a number operator \( \psi_p^\dagger \psi_p \) in the expression for \( \psi(L_\alpha^\alpha) \), is a sum of one electron operators and cannot excite higher molecular spin states. Consequently, only excited states \( \psi_p \), as given in expression (5-13), can contribute to \( \psi(L_\alpha^\alpha) \), if we neglect overlap effects (see below). Substituting expressions (5-12) and (5-13) in the expression for \( \psi(L_\alpha^\alpha) \) we obtain:

\[ \psi(L_\alpha^\alpha) = \sum \frac{1}{\sqrt{C_p}} \frac{1}{\sqrt{C_p}} \left| \psi_1(1) \psi_2(2) \psi_3(3) \psi_4(4) \ldots \ldots \right| \]

\[ \psi_p = \frac{1}{\sqrt{C_p}} \left| \psi_1(1) \psi_2(2) \psi_3(3) \psi_4(4) \ldots \ldots \right| \]

(5-14)

where \( E_p \) is the energy of the excited molecular electronic state \( \psi_p \). The factor 2 arises as there are two electrons in each occupied MO.

Substituting Eq. (5-13) into expression (5-14) gives:

\[ \psi(L_\alpha^\alpha) = \sum \frac{1}{\sqrt{C_p}} \frac{1}{\sqrt{C_p}} \left| \psi_1(1) \psi_2(2) \psi_3(3) \psi_4(4) \ldots \ldots \right| \]

\[ \psi_p = \frac{1}{\sqrt{C_p}} \left| \psi_1(1) \psi_2(2) \psi_3(3) \psi_4(4) \ldots \ldots \right| \]

(5-15)

The sums over \( i \) and \( p \) are over the occupied and unoccupied molecular orbitals. \( L_\alpha^{(K)^\alpha}_\Sigma \) represents \( \psi(L_\alpha^\alpha) \). Thus, if the MO's are known in terms of atomic orbitals the paramagnetic susceptibility can be calculated from Eq. (5-15) by evaluating \( \langle \psi_p(L_\alpha^\alpha) | \psi_p(L_\alpha^\alpha) \rangle \) for the various atomic orbitals in the molecule. All matrix elements of the \( L_\alpha^\alpha \), \( \psi_\alpha^\alpha \), and \( L_\alpha^\alpha \) operators involving the spherically symmetric g electronic functions are zero. In addition overlap integrals between two atomic centers will be small and can generally be neglected (Pop 62, Fox 63).

A further simplification can be made if the inverse excitation energy factors \( \psi(L_\alpha^\alpha) \) and \( \psi(L_\alpha^\alpha) \) are replaced by a mean value \( \bar{E} \). In this case the summation over \( i \) and \( p \) can be put in a more explicit form if the type of the involved atomic orbitals is considered in detail. This will be shown below for water using the model of Ellison and Wall (All 55) for the electronic structure of the water molecule. This model includes only \( L_\alpha^\alpha \) orbitals at the proton and 1s, 2s and 2p orbitals at the oxygen nucleus. The 2p orbitals have the same radial function. The result of operating on these functions by a component of \( L_\alpha^\alpha \) is given below for the case of the oxygen nucleus:

\[ L_\alpha^\alpha \left[ \psi_p \right] = ip_p \psi_p \]

\[ L_\alpha^\alpha \left[ \psi_p \right] = -ip_p \psi_p \]

\[ L_\alpha^\alpha \left[ \psi_p \right] = 0 \]
Substituting expression \((5-16)\) into \((5-15)\) we get:

\[
\Gamma(0, ^0_2) = \frac{4\pi^2}{3} \delta_{10}^2 \sum I \left( c_{12}^\ast c_{11}^\ast c_{21} c_{12} \right) \delta_{12}^2 \left( c_{12}^\ast c_{12} - c_{11}^\ast c_{11} - c_{21}^\ast c_{22} - c_{22}^\ast c_{21} \right), \tag{5-17}
\]

where \(c_{ij}\) is the coefficient in Eq. \((5-11)\) for the \(p_x\) atomic orbital at oxygen for the occupied \(i\)-th MO.

The summation over \(i\) and \(p\) can then be expressed in terms of the population density matrix \(P_{\mu\nu}\):

\[
P_{\mu\nu} = \sum \delta_{\mu\nu}^0 c_{i\mu} c_{i\mu}^\ast. \tag{5-18}
\]

In the approximation neglecting overlap integrals we have:

\[
\delta_{\mu\nu}^0 c_{i\mu}^\ast c_{i\nu} = \delta_{\mu\nu}^0 c_{i\mu}^\ast c_{i\nu}. \tag{5-19}
\]

Application of Eq. \((5-18)\) and \((5-19)\) in expression \((5-17)\) gives:

\[
\Gamma(0, ^0_2) = \frac{16\pi^2}{3} \left( P_{xx} + P_{xy} + P_{yx} + P_{yy} - P_{yx} - P_{yy} \right). \tag{5-20}
\]

Using coefficients \(c_{i\mu}\) of Ellison and Shell and substituting the ionization energy for \(\delta\) we get the values for \(\Gamma(0, ^0_2)\) given in the last column of Table \(5-4\). Comparison with experimental values shows that the theoretical values are too large by about a factor of three. The failure of the theory can be due both to the electronic model of Ellison and Shell as well as to the several simplifications made in the derivation of Eq. \((5-20)\).

Similar discrepancies between approximate theory and experiment are also reported for other molecular systems (Fly 64a).

### 5.3.3 Relationship between molecular g-values and nuclear spin-rotation coupling constant

Assuming that the \(r^{-3}\) term can be extracted parametrically, the electronic contribution (see Table \(5-1\)) to the spin-rotation interaction (Whi 55) is:

\[
\frac{\chi(K)}{6 \mu} = -\frac{4\pi^2}{3} \delta_{10}^2 \sum I \left( c_{12}^\ast c_{11} c_{21} c_{12} \right) \delta_{\mu\nu}^2 \left( c_{12}^\ast c_{12} - c_{11}^\ast c_{11} - c_{21}^\ast c_{22} - c_{22}^\ast c_{21} \right), \tag{5-21}
\]

where \(\chi^{-3}\) is assumed to be the average value of \(r^{-3}\) between the ground and the \(k\)-th electronic state of the molecule, with the origin of \(r\) at the \(K\)-th nucleus. The sum appearing in Eq. \((5-21)\) is discussed in Sect. 5.3.2 and the numerical values are given in Table \(5-4\).

There are two important approximations made in extracting \(r^{-3}\).

They are the assumptions that \(\langle 0 | r^{-3} | n \rangle\) is equal to the product of \(\langle 0 | r^{-3} | n \rangle\) and \(\langle 0 | r^{-3} | n \rangle\), and that \(\langle 0 | r^{-3} | n \rangle\) is the same for all \(n\) or that one single term is dominant. The parametric value of \(\langle 0 | r^{-3} | n \rangle\), abbreviated as \(r^{-3}\), can be obtained from Eq. \((5-13)\) if one knows the electronic contribution to the spin-rotation term.

The values of \(\chi(K)(e)\) at the deuteron are determined from the measured spin-rotation constants (Blu 67a) and the calculated nuclear contribution. The resulting values for \(\chi(K)(e)\) at the deuteron are [in \(\text{kg}^{-1}\text{m}^{-2}\)]:

\[
\begin{align*}
\chi_{aa}^{(0)} (e) &= 9.583 \times 10^{38} \\
\chi_{bb}^{(0)} (e) &= 6.63 \times 10^{38} \\
\chi_{cc}^{(0)} (e) &= 5.685 \times 10^{38}
\end{align*}
\]

Substitution of these values into Eq. \((5-21)\) yields the following results for \(r^{-3}\) in units of \(\text{m}^{-3}\):

\[
\begin{align*}
g &= 9.6 \times 10^{39} \\
g &= 8.3 \times 10^{39} \\
g &= 8.6 \times 10^{39}
\end{align*}
\]

These values agree mutually to within about 15% and hence one may assume a parametric value for \(r^{-3}\) of \(9 \times 10^{29} \text{ m}^{-3}\) as the characteristic value for the deuteron and proton in water.

It is shown in Sect. 5.2 that the tensor elements \(\chi_{ij}(e)\) cannot be obtained from the experimental results because only two values of \(\chi_{ij}(0)\) are known. In the case of the 2\(_1\) level of HD\(^{17}O\) the expression for \(\chi_{ij}(0)\) \((\text{Table 3-2})\) reads:

\[
\begin{align*}
\chi_{ij}(0) &= \sum_{\text{a}_1}^{\text{a}_2} \sum_{\text{b}_1}^{\text{b}_2} \sum_{\text{c}_1}^{\text{c}_3} \sum_{\text{d}_1}^{\text{d}_3} \sum_{\text{e}_1}^{\text{e}_3} \sum_{\text{f}_1}^{\text{f}_3} \sum_{\text{g}_1}^{\text{g}_3} \sum_{\text{h}_1}^{\text{h}_3} \text{ terms}
\end{align*}
\]

\[
\begin{align*}
\chi_{ij}(0) &= \sum_{\text{a}_1}^{\text{a}_2} \sum_{\text{b}_1}^{\text{b}_2} \sum_{\text{c}_1}^{\text{c}_3} \sum_{\text{d}_1}^{\text{d}_3} \sum_{\text{e}_1}^{\text{e}_3} \sum_{\text{f}_1}^{\text{f}_3} \sum_{\text{g}_1}^{\text{g}_3} \sum_{\text{h}_1}^{\text{h}_3} \text{ terms}
\end{align*}
\]
and the numerical value is $C_{0}^{(0)} = -22.35(22)$ kHz; $a, b$, and $c$ represent the principal inertial axes of HD$^{17}$O. Substituting expression (5-21) into expression (5-24) gives:

$$C_{0}^{(0)}(n) = \frac{e^{-2}}{r^{3}} \left( \frac{a_{a}^{2}}{a_{a}^{2}} \right) + \frac{e^{-2}}{r^{3}} \left( \frac{b_{b}^{2}}{b_{b}^{2}} \right) + \frac{e^{-2}}{r^{3}} \left( \frac{c_{c}^{2}}{c_{c}^{2}} \right)$$ (5-25)

The values for $C_{0}^{(0)}(n)$ are calculated from the nuclear geometry. Consequently, $e^{-2}$ can be calculated from the values of $\frac{C_{0}^{(0)}}{e}$ given in Table 5-1:

$$e^{-2} = 1.63 \times 10^{-4} \text{ m}^{-2}$$ (5-26)

This value should be compared with the value calculated with ground state atomic orbitals of the 0-atom $\psi_{0}^{(0)}|e^{-2}|0^{0} = 2.81 \times 10^{-4} \text{ m}^{-2}$. A possible reason for the smaller value given in Eq. (5-26) is that the electron density distribution of a ground and an excited orbital differ substantially. The matrix elements of $\frac{1}{r^{2}}$ between a ground state and an excited state wave function will therefore generally be smaller than the expectation value for the ground state. In view of this it is not surprising that the expectation value of $\frac{1}{r^{2}}$ for the ground state of oxygen is larger than the value quoted in Eq. (5-26).

5.3.4 Relationship between molecular magnetic moments of D$_{2}$O, HDO, and H$_{2}$O

The sign of the molecular electric dipole moment

The electric dipole moment of 1.85(2) D of water has been determined from the Stark effect on the rotational states (Nel 67). However, this method yields only the magnitude of the moment and not the sign.

It was first shown by Tomsen et al. (Tov 55a) that the sign of the electric dipole moment can be obtained from the isotopic dependence in the molecular g-values. The appropriate equation relating the g-values to the dipole moment is (Tov 55a, Nel 68, Neu 68):

$$\left[ \begin{array}{c} g_{g} \\ A_{g} \\ \end{array} \right] = \left[ \begin{array}{c} g_{g} \\ A_{g} \\ \end{array} \right] + \frac{2}{g} \left( \bar{B}_{g} - \left(g_{g} \frac{\Delta g}{g} \right) \right)$$ (5-27)

where the subscripts $\frac{1}{2}$ and $\frac{3}{2}$ indicate the initial and the final isotope, respectively; $\mu_{g}$ represents the $g$-th component of the electric dipole moment assumed to be along the symmetry axis of the molecule, and $\Delta g$ is the change in position of the center of mass because of the isotopic substitution, referred to the coordinate system of the initial isotopic species. In the derivation of Eq. (5-27) it is assumed that the nuclear and electronic charge distribution are invariant under isotopic substitution.

Using Eq. (5-27) with H$_{2}$O as the final molecule and D$_{2}$O as the initial molecule, we get the following relations:

$$g_{AA}(H_{2}O) = 1.91072 g_{AA}(D_{2}O) - 0.01028 \mu$$
$$g_{bb}(H_{2}O) = 1.9993 g_{bb}(D_{2}O)$$
$$g_{cc}(H_{2}O) = 1.9165 g_{cc}(D_{2}O) - 0.01208 \mu$$ (5-28)

Substituting Eq. (5-28) into the expression for the molecular magnetic moment of H$_{2}$O (Table 3-2) we obtain:

$$J(4+1) \times 8_{g} = 1.81265 e^{-2} g_{AA}(D_{2}O) + 1.9993 e^{-2} g_{bb}(D_{2}O) + 1.9165 e^{-2} g_{cc}(D_{2}O) - 0.01208 e^{-2} \mu$$ (5-29)

Using the experimental values of $g_{g}$ and $g_{g}$ (Table 3-4) and the known values of $e^{-2}$ and $g_{AA}(D_{2}O)$ the following values for the dipole moment are obtained:

$$g_{AA}(D_{2}O) \text{ level} \ldots \mu = -1.96(5) \text{ D}$$
$$g_{BB}(D_{2}O) \text{ level} \ldots \mu = -1.70(8) D$$ (5-30)

To relate the $g_{g}$ values of HDO and D$_{2}$O we must transform the $g_{AA}(D_{2}O)$ from the $g$-axle of D$_{2}$O to the $g$-axle of HDO. This is performed by a rotation (O. H. Beh. behaves like the product of two vectors) and a translation as given in Eq. (5-27). The resulting expressions are:

$$g_{AA}(\text{HDO}) = 1.3236 g_{AA}(D_{2}O) + 0.4178 g_{bb}(D_{2}O) - 0.39038 \mu$$
$$g_{bb}(\text{HDO}) = 0.07388 g_{bb}(D_{2}O) + 1.0993 g_{bb}(D_{2}O) + 0.00232 \mu$$
$$g_{BB}(\text{HDO}) = 1.3234 g_{bb}(D_{2}O) + 0.02396 \mu$$ (5-31)
The values of the electric dipole moment calculated from the molecular g-values of D₂O and D₂ are:

\[ \mu = -1.53(2) \text{ D} \]

\[ \mu = -1.54(2) \text{ D} \]  \hspace{1cm} (5-32)

The experimental dipole moment of 1.85 D is outside the range of the values calculated from the g-values of D₂O and H₂O (Eq. (5-30)) and D₂O and HDO (Eq. (5-32)). This is especially evident for the combination D₂O - HDO. A change in the g-values of H₂O by 0.2 % and of HDO by about one percent would change the values given in Eq. (5-30) and (5-32) in such a way that these discrepancies are removed.

The rather large discrepancies indicate a breakdown of the assumed invariance of the nuclear and electronic charge distribution with isotopic substitution. This may be caused by several effects among which centrifugal distortion and vibrational effects are the most probable ones. The agreement between the experimental and calculated magnetic moments of D₂O, as discussed in Sect. 5.2.1, indicates that centrifugal distortion has no measurable influence on the g\(^{(e)}\)-values of D₂O up to J = 5. The effect of centrifugal distortion on the g\(^{(e)}\)-values of HDO and H₂O may be somewhat larger but can also be neglected.

The effect of centrifugal distortion on g\(^{(n)}\) is estimated from the results on centrifugal distortion obtained by Posener and Strandsberg (Pos 54). This effect is found to be too small to explain the discrepancies between the molecular tensors of HDO, D₂O and H₂O. However, the zero point vibration of the molecule has to be taken into account, especially for the effects of isotopic substitutions on the anharmonic terms in the potential function.

Using the experimental data of Benedikt et al (Ben 56), Kuchitsu and Bartell (Kuc 62) and also Kern (Ker 68) calculated the vibrational displacements in several isotopic species of the water molecule.

These displacements are generally rather large, for example, the angle between the two OH-bonds varies by about 10 % in H₂O (Fig. 5-2). The displacements due to zero-point vibrations are shown in Table 5-5 for a number of isotopic molecules. The quantity ΔR(0-H) represents the shift in the equilibrium distance between O and H because of the anharmonic terms in the molecular potential; \( \langle 4x^2 \rangle \) is the mean square value of the deviation of the x coordinate. It is seen from Table 5-5 that the overall change in the nuclear geometry, because of zero-point shifts, is about 1 Å.

<table>
<thead>
<tr>
<th></th>
<th>H₂O</th>
<th>D₂O</th>
<th>HDO</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔR(0-H)</td>
<td>0.0148</td>
<td>0.0107</td>
<td>0.0149</td>
<td>Ker 68</td>
</tr>
<tr>
<td>ΔR(0-D)</td>
<td>-0.29</td>
<td>-0.14</td>
<td>-0.15</td>
<td>Ker 68</td>
</tr>
<tr>
<td>( \langle (R-R)_{(e)}^2 \rangle )</td>
<td>0.069</td>
<td>0.039</td>
<td></td>
<td>Kuc 62</td>
</tr>
<tr>
<td>( \langle (\Delta x)^2 \rangle )</td>
<td>0.074</td>
<td>0.063</td>
<td></td>
<td>Kuc 62</td>
</tr>
<tr>
<td>( \langle (\Delta y)^2 \rangle )</td>
<td>8.720</td>
<td>7.490</td>
<td></td>
<td>Kuc 62</td>
</tr>
</tbody>
</table>

Table 5-5. Zero-point vibrational corrections and mean changes of the internal coordinates of H₂O, D₂O, and HDO. R\(_e\) is the equilibrium distance of R(0-H), respectively, R(0-D); see Fig. 5-2. All distances are given in units of 10\(^{-10}\) m.

Fig. 5-2. The internal coordinates of the water molecule.

Calculation of the nuclear part of the g-tensor, performed by us, shows that inclusion of the zero point shifts as a correction to the rigid rotor model for the three isotopic species does not remove the discrepancies in the g-values mentioned above (Ver 69a). By consequence these discrepancies have to be explained by the zero-point effects on the electronic part and by higher order vibration effects on the magnetic tensor.
Chan, Ikenberry, and Das (Cha 54) and Russell (Rus 62) investigated the determination of electric dipole moments of diatomic molecules from rotational magnetic moments of isotopic species. They pointed out that appreciable errors in the dipole moment can result if one neglects the effects of vibrational motion on the paramagnetic part of the magnetic moment tensor. This agrees with our findings for the water molecule.

Assuming that the rigid rotor model explains the values of the G-tensor elements to within one percent, the $G_{aa}$ values of D$_2$O and H$_2$O are calculated from the $G_{aa}$ values of D$_2$. These values are listed in Table 5-6 and compared with the values calculated by Burke and Strandberg (Bur 53) and Schwarz (Sch 52) from experimental data obtained with a conventional Zeeman spectrometer. Deviations are about two per cent with one exception: the $G_{aa}$ values of D$_2$ differ by about 10%. A reason for the discrepancies can be the low resolving power of the conventional Zeeman spectrometer and the neglect of hyperfine interactions in the analysis of spectra.

<table>
<thead>
<tr>
<th></th>
<th>Burke and Strandberg (Bur 53)</th>
<th>Schwarz (Sch 52)</th>
<th>The present work</th>
</tr>
</thead>
<tbody>
<tr>
<td>D$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$G_{aa}$</td>
<td>0.363</td>
<td>0.287</td>
<td>0.32530(10)</td>
</tr>
<tr>
<td>$G_{bb}$</td>
<td>0.252</td>
<td>0.271</td>
<td>0.36009(22)</td>
</tr>
<tr>
<td>$G_{cc}$</td>
<td>0.332</td>
<td>0.336</td>
<td>0.32513(20)</td>
</tr>
<tr>
<td>H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$G_{aa}$</td>
<td>0.685</td>
<td>0.585</td>
<td>0.657(7)</td>
</tr>
<tr>
<td>$G_{bb}$</td>
<td>0.707</td>
<td>0.702</td>
<td>0.718(7)</td>
</tr>
<tr>
<td>$G_{cc}$</td>
<td>0.650</td>
<td>0.666</td>
<td>0.665(6)</td>
</tr>
<tr>
<td>HDO</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$G_{aa}$</td>
<td>0.623</td>
<td>0.589</td>
<td>0.618(6)</td>
</tr>
<tr>
<td>$G_{bb}$</td>
<td>0.438</td>
<td>0.460</td>
<td>0.413(4)</td>
</tr>
<tr>
<td>$G_{cc}$</td>
<td>0.413</td>
<td>0.430</td>
<td>0.437(4)</td>
</tr>
</tbody>
</table>

Table 5-6. Molecular $G_{aa}$ values of D$_2$O, H$_2$O, and HDO

For a better understanding of vibrational effects it is of interest to measure magnetic moments of excited vibrational levels. This is difficult, however, because the fraction of molecules in the first excited vibrational level is only about 0.2%. The expected signal to noise ratio at this low population is beyond the sensitivity of the present spectrometer.

In view of vibrational effects the discrepancies in the calculation of the magnitude of the dipole moments from measured $g$-values for different isotopic species of the water molecule are not surprising.

However, the sign of the dipole moment can well be determined. Let us assume, for example, that the dipole moment is positive in contrast to the values given in Eqs. (5-30) and (5-32). Then the corresponding deviation from the rigid rotor model due to vibrational effects will have unreasonable values of up to 12%. In that case one may also expect large deviations from the isotopic invariance of the deuterium quadrupole coupling tensor and the proton, spin-rotation interaction tensor, in contrast to the observations (Blu 67, Sect 4.3.1). Consequently it is clear that the sign of the dipole moment is negative, i.e. the polarity is $O^-$ rather than $O^+$. As expected.

5.4 THE MOLECULAR MAGNETIC SUSCEPTIBILITY TENSORS

5.4.1 Anisotropies in the diagonal elements of D$_2$O

It is shown in Sect 3.3 that the coupling constants of the molecular susceptibility are expressed in terms of the diagonal tensor elements:

$$x_{ij} = \frac{1}{6} \frac{\omega_{ij}^2}{\Omega^2} (x_{gg} - x_{uv}),$$

with

$$x_{gg} = \chi_{gg} + \chi_{uv}.$$

Consequently only the anisotropies of the magnetic susceptibility can be obtained from the experimental results. The values for $(x_{gg} - x_{uv})$ are calculated by means of a least squares fit from the measured coupling constants of the levels $2_g$, $3_g^1, 4_g^3$, and $5_g$ of D$_2$O. The resulting values for D$_2$O are (in kHz$^{-2}$):

$$x_{gg} - x_{uv} = 3.88(20) \times 10^{-5},$$
In order to compare these results with the values calculated from theoretical density distributions, the tensor components $\chi_{gg}$ of $D_2^0$ are transformed to the molecular system of $H_2O$. As follows from the definitions and also from physical arguments, isotopic substitution will not change the $\chi$-tensor in the rigid rotor model. However, both the diamagnetic and the paramagnetic part change with isotopic substitution. The changes in $\chi_{gg}^{(a)}$ can easily be derived from the definition (Table 3-1). The result is:

$$\chi_{gg}^{(a)}(H_2O) = \chi_{gg}^{(a)}(D_2O) + \frac{2}{3} \mu_B^2 \langle \hat{S}(\hat{S})_z \rangle_0 \langle F(\hat{F})_z \rangle_0 + \frac{1}{3} \delta(\epsilon, \sigma) \delta(\epsilon, \sigma)$$

where $(\hat{F})_z$ is the $z$-th component of the position vector of the $i$-th electron with respect to the center of mass of $H_2O$; $\tilde{I}$ is the position vector of the center of mass of $H_2O$ with respect to the center of mass of $D_2O$. $\epsilon_{1i}$ is the number of electrons. The value of $\langle \hat{S}(\hat{S})_z \rangle_0 \delta(\epsilon, \sigma) \delta(\epsilon, \sigma)$ can be calculated from the electric dipole moment of the molecule. With $\mu_B = 0.57$ D we get from Eq.(5-37) in units of kHzs$^{-2}$:

$$\chi_{gg}^{(a)}(H_2O) = \chi_{gg}^{(a)}(D_2O) + 0.14 \times 10^{-7}$$

The resulting values for $\chi_{gg}^{(a)}(H_2O)$ and $\chi_{gg}^{(a)}(D_2O)$ in the $H_2O$-system are given in Table 5-7, together with the theoretical values.

### 5.4.2 Molecular quadrupole moment and anisotropies in the average values of the squared electronic coordinates

According to the definition (Table 3-1) the anisotropy in the diamagnetic part of the susceptibility tensor can be written as:

$$\chi_{gg}^{(a)} = \frac{\mu_B^2}{3} \langle \hat{S}(\hat{S})_z \rangle_0 \langle F(\hat{F})_z \rangle_0 - (\hat{F}_z)^2 \rangle_0$$

The anisotropies in the diamagnetic part are then calculated from Eqs. (5-33) and (5-35):

$$\chi_{gg}^{(a)} = 2.33(2) \times 10^{-7} \text{ kHzs}^{-2}$$

$$\chi_{bb}^{(a)} = 0.37(4) \times 10^{-7} \text{ kHzs}^{-2}$$

$$\chi_{cc}^{(a)} = 2.69(3) \times 10^{-7} \text{ kHzs}^{-2}$$

Comparison of the measured and best-fit values shows a good fit (Ver 69a).
The operator
\[ \sum_{i} \left( \langle \mathbf{F}_{i}^{2} \rangle - \langle \mathbf{F}_{i} \rangle^{2} \right) \]
represents clearly a measure of the deviation of the charge distribution from spherical symmetry.

Using for \( \chi_{\alpha \beta} = \chi_{\alpha \beta} \) of \( \text{H}_2\text{O} \) the values given in Table 5-7 we get for the anisotropies in the second-order moments of the electronic charge distribution (in units of \( 10^{-21} \text{m}^2 \)):

\[ <0|\sum_{i} \left( \langle \mathbf{F}_{i}^{2} \rangle - \langle \mathbf{F}_{i} \rangle^{2} \right)|0> = -7.45(9) \]

\[ <0|\sum_{i} \left( \langle \mathbf{F}_{i}^{2} \rangle - \langle \mathbf{F}_{i} \rangle^{2} \right)|0> = 6.71(6) \]

\[ <0|\sum_{i} \left( \langle \mathbf{F}_{i}^{2} \rangle - \langle \mathbf{F}_{i} \rangle^{2} \right)|0> = 0.76(12) \]  \( (5.40) \)

Other anisotropies, like \( <0|\sum_{i} \left( \langle \mathbf{F}_{i}^{2} \rangle - \langle \mathbf{F}_{i} \rangle^{2} \right)|0> \), can similarly be calculated from Eq. (5.40). These values do not provide an independent test on the calculated charge distribution, and will not be discussed.

Another molecular quantity of interest, the molecular quadrupole tensor, is also related to the data obtained above. This tensor is defined as:

\[ \theta_{\alpha \beta} = -\frac{1}{2} \sum_{i} <0|\sum_{i} \left( \langle \mathbf{F}_{i}^{2} \rangle - \langle \mathbf{F}_{i} \rangle^{2} \right)| \mathbf{g}_{\alpha \beta} |0> = \frac{1}{2} \sum_{i} \left( \langle \mathbf{F}_{i}^{2} \rangle_{\alpha \beta} - \langle \mathbf{F}_{i}^{2} \rangle \right) \mathbf{g}_{\alpha \beta} \]  \( (5.41) \)

The nuclear term is easily computed from the geometry of the molecule. The electronic contribution can be calculated using known wave functions of the electronic ground state. Such "ab-initio" calculations have been performed recently by several authors for the water molecule (see Sect. 5.4-6). Until now there was no experimental value for this quantity.

The off-diagonal elements of the quadrupole tensor of \( \text{D}_2\text{O} \) are zero by symmetry requirements. The diagonal elements can be obtained directly from the present values of the molecular magnetic moment and the anisotropies in the magnetic susceptibility.

As follows from the definition of the molecular magnetic moment tensor, the susceptibility tensor (Table 3-1), and of the quadrupole tensor we have:

\[ \theta_{\alpha \beta} (\text{D}_2\text{O}) = \theta_{\alpha \beta} (\text{H}_2\text{O}) - \lambda_{\beta \beta} \delta_{\alpha \beta} \]  \( (5.42) \)

The experimental values of \( \chi_{\alpha \beta} \) and \( \theta_{\alpha \beta} \) are given in Sects. (5.4-1) and (5.3.1). Substitution of these values yields the following quadrupole tensor elements of \( \text{D}_2\text{O} \) (in units \( 10^{-26} \text{ esu cm}^2 \)).

\[ \theta_{aa} = 2.72(14) \]
\[ \theta_{bb} = -0.32(7) \]
\[ \theta_{cc} = -2.40(21) \]  \( (5.43) \)

In order to compare these results with theoretical values, the former ones are transformed to the \( \text{H}_2\text{O} \)-axes system using the relation:

\[ \theta_{\alpha \beta} (\text{H}_2\text{O}) = \theta_{\alpha \beta} (\text{D}_2\text{O}) - (3\delta_{a b} \delta_{\alpha \beta} - 3-\delta_{\alpha \beta} \lambda_{a a} \lambda_{b b} \lambda_{c c}) \]  \( (5.44) \)

which can be derived from Eqs. (5.42), (5.47) and (5.37). By substituting \( \lambda_{\alpha \alpha} = 1.85(2) \) in Eq. (5.44) we get (in the same units):

\[ \theta_{aa} (\text{H}_2\text{O}) = \theta_{aa} (\text{D}_2\text{O}) - 0.096 \]
\[ \theta_{bb} (\text{H}_2\text{O}) = \theta_{bb} (\text{D}_2\text{O}) + 0.192 \]
\[ \theta_{cc} (\text{H}_2\text{O}) = \theta_{cc} (\text{D}_2\text{O}) - 0.096 \]  \( (5.45) \)

The values of \( \theta_{\alpha \beta} (\text{H}_2\text{O}) \), obtained by substitution of Eq. (5.43) into Eq. (5.45), and the results of ab-initio calculations are given in Table 5-7.

5.4.3 Average values of the squared electronic coordinates

The average diamagnetic susceptibility is directly proportional to the value of \( <0|\mathbf{F}_{i}^{2}|0> \).
\[
\chi_{av} = -\frac{2.2}{30} \text{m}^3 <0|\mathbf{F}_1^2|0>.
\]  
(5.46)

This relation is easily derived using the definition (Table 3-2) of \(\chi_{av}\). The average diamagnetic susceptibility can be calculated from the average magnetic susceptibility and the average paramagnetic susceptibility.

The average paramagnetic susceptibility of \(\text{H}_2\text{O}\) can be calculated from the values of Eqs. (5-36) and (5-38), using the fact that \(\chi_{av}\) is invariant under isotopic substitution. The resulting value for \(\text{H}_2\text{O}\) is:

\[
\chi_{av} = 3.88 \times 10^{-7} \text{ KHz G}^{-2}.
\]  
(5.47)

As shown in Sect.4.2 the average magnetic susceptibility or bulk susceptibility cannot be measured in beam experiments. To our knowledge no experimental value for \(\chi_{av}\) is known in the literature. The value may be calculated semi-empirically by means of Pascal rules (Bel 56).

Assuming that the magnetic susceptibilities of gaseous and liquid phase are the same to within 15 \%, Eisenberg et al. (Ris 65) assigned to the average susceptibility the value:

\[
\chi_{av} = -3.26(50) \times 10^{-6} \text{ KHz G}^{-2}.
\]  
(5.48)

By consequence the average diamagnetic susceptibility of \(\text{H}_2\text{O}\) is:

\[
\chi_{av}^{(d)} = -3.65(50) \times 10^{-6} \text{ KHz G}^{-2},
\]

and the corresponding average value for the squared electronic coordinates (using Eq. (3-46)):

\[
<0|\mathbf{F}_1^2|0> = 5.15(70) \times 10^{-20} \text{ m}^2.
\]  
(5.49)

This result is compared in Sect.5.6 with theoretical values.

Combination of Eq. (5-49) and (5-40) gives values for the squared components of the electronic coordinates in \(\text{H}_2\text{O}:

\[
<0|\mathbf{F}_1^2|0> = 1.47(20) \times 10^{-20} \text{ m}^2,
\]

\[
<0|\mathbf{F}_1^2|0> = 1.94(20) \times 10^{-20} \text{ m}^2,
\]

\[
<0|\mathbf{F}_1^2|0> = 1.74(20) \times 10^{-20} \text{ m}^2.
\]  
(5.50)

These values may also be used to test the calculated electronic charge distribution. However, because of the large uncertainty introduced in Eq. (5-48), the results represents a rather weak criterion compared with the anisotropies given in Eq. (5-40) and will therefore not further be considered.

5.4.4 Relationship between the magnetic susceptibility tensors of \(\text{HDO}\) and \(\text{D}_2\text{O}\)

As shown in Sect.5.4.1 the \(\chi\)-tensor is invariant with respect to isotopic substitution in the rigid rotor approximation. By consequence the components of this tensor in the principal system of reference of \(\text{HDO}\) can be obtained from the tensor components of \(\text{D}_2\text{O}\) in its principal system of reference by a rotation.

The coupling constant \(\chi_{fr}^2\) is calculated in this way for the \(2\) and \(2\), levels of \(\text{HDO}\) from the values of \((\chi_{fr}^2 - \chi_{av}^2)\) of \(\text{H}_2\text{O}\) given in Eq. (5-36). The resulting values are (in units of \(10^{-8}\text{KHz G}^{-2}\)):

\[
\chi_2' = 1.63(11),
\]

\[
\chi_2 = 1.58(101),
\]  
(5.51)

Comparison with the measured values (Table 4.1)(in the same units):

\[
\chi_2' = 1.73(15),
\]

\[
\chi_2 = 1.83(15),
\]  
(5.52)

shows a good agreement for the \(\chi_2'\) value and a deviation about twice the experimental error for \(\chi_2\). This deviation can be explained by breakdown of the rigid rotor approximation as follows.
The values of the anisotropy in the diagonal components of the x-tensor are about three percent of the value of the diagonal components. From the observed deviations of the components of the G-tensor from the rigid rotor model (Sect. 5.3.4), we may assume that the variation of the components of the x-tensor on isotopic substitution is of the order of one percent. In this case large deviations can occur in the anisotropies of these elements for the isotopic species.

5.5 THE MAGNETIC SHIELDING TENSORS

The paramagnetic components of the nuclear shielding tensor given in Table 4-5 are easily calculated from the electronic contribution to the nuclear spin-rotation interaction, using a relation which is easily derived from the definitions of the involved tensors (Table 3-1):

\[
\sigma_{\text{av}}(K) = \frac{-\mu_K^2 H_0 M_{\text{av}}(K)M_{\text{av}}(e)}{2g_K g_e \mu_B H_0 M_{\text{av}}(K)}. \tag{5-53}
\]

With the value for \(M_{\text{av}}(e)\) given in Eq. (5-22) and the values for \(g_K\) from Table 5-1 we obtain for the deuteron shielding:

\[
\begin{align*}
\sigma_{\text{av}}^{(d)}(\text{aa}) &= -37.3 \times 10^{-6}, \\
\sigma_{\text{av}}^{(d)}(\text{bb}) &= -71.3 \times 10^{-6}, \\
\sigma_{\text{av}}^{(d)}(\text{cc}) &= -108.3 \times 10^{-6}. \tag{5-54}
\end{align*}
\]

For \(\sigma_{\text{av}}^{(d)}\) we obtain from these values:

\[
\sigma_{\text{av}}^{(d)} = -75.2 \times 10^{-6}. \tag{5-55}
\]

The average paramagnetic shielding may be combined with the average total magnetic shielding in order to obtain the ground state dependent average diamagnetic shielding. Unfortunately, the isotropic magnetic shielding cannot be measured in this experiment. Using the values obtained from nuclear magnetic resonance experiments (Top 59):

\[
\sigma_{\text{av}}^{(d)} = 30.2 \times 10^{-6}. \tag{5-56}
\]

we get for the diamagnetic part:

\[
\sigma_{\text{av}}^{(d)} = 102.4 \times 10^{-6}. \tag{5-57}
\]

Several authors calculated this quantity. The results of these calculations will be discussed in Sect. 5.6.2.

The paramagnetic contribution to \(\sigma_{3}^{(d)}\) of any level of \(D_0\) can be calculated from the values given in Eq. (5-54). For example, in case of the \(\eta_3\) level this contribution \(\sigma_{3}^{(d)}(\text{p})\) is:

\[
\sigma_{3}^{(d)}(\text{p}) = 28 \times 10^{-6}. \tag{5-58}
\]

From this value and the measured value of \(\sigma_{3}^{(d)}\) given in Table 4-4:

\[
\sigma_{3}^{(d)} = -12(4) \times 10^{-6}, \tag{5-59}
\]

the diamagnetic contribution is easily calculated:

\[
\sigma_{3}^{(d)} = -10(4) \times 10^{-6}. \tag{5-60}
\]

This value may be compared with the value calculated from the ground state electron state of the water molecule. However, until now no calculated values for the anisotropy of the components of the diamagnetic shielding tensor of the proton (deuteron) in water are published. For this reason, the \(\sigma_{3}^{(K)}\), which have large experimental errors as can be seen in Table 4-4, are not further analyzed.

In view of this it is desirable to include in future calculations of the one electron properties of water also the individual components of the diamagnetic shielding tensor of the proton in order to test the quality of the calculated charge distribution.

No experimental values of the average magnetic shielding and of the spin-rotation tensor elements of oxygen are available. Consequent-
ly the calculated average diamagnetic oxygen shielding cannot be compared with an experimental value.

5.6 DISCUSSION

5.6.1 Review of calculations of one electron properties of the water molecule with several LCAO-MO-SCF ground state functions

Ellison and Shull (Ref 55) were the first to make accurate calculations on the water molecule in its ground state. Several previous treatments used approximate valence bond methods (Cox 38, Vio 34, Pau 37). Ellison and Shull's calculations were based on the Hooftaan's mathematical formulation of the self consistent field (SCF) molecular orbital theory (Ref 51), using a linear combination of atomic orbitals (LCAO) for each molecular orbital (MO). They used the familiar Born-Oppenheimer (BO) approximation without relativistic corrections for the Hamilton operator. To make use of the symmetry properties of the MO's, it is convenient to introduce symmetry orbitals. These are linear combinations of AO's taken so as to belong to irreducible representation of the symmetry group of the molecule. As the water molecule belongs to the group \( C_2v \), the irreducible representations are designated by \( a_1 \), \( a_2 \), \( b_1 \), and \( b_2 \). According to Ellison and Shull's calculation, the electronic configuration of the ground state of the molecule is (Ref 55):

\[ \psi = \frac{1}{\sqrt{2}} (a_1 \psi_1 + b_2 \psi_2) \]

This is a singlet state \( ^1 \Sigma \) belonging to a totally symmetric group representation.

Ellison and Shull used a minimal basis set of Slater type orbitals (STO) centered at the various nuclei to construct SCF-LCAO-MO'S. This treatment was followed by the work of McWeeny and Ohno (Ref 60) who, using the same basis set, checked the results of Ellison and Shull and tried a few other methods. Merrifield (Ref 62) used also the method of Ellison and Shull but with more accurate three-centre integrals.

In order to alleviate some of the computational difficulties with many-centre integrals, several other choices of basis sets were used. Bishop and Randic (Ref 66) and Moccia (Ref 64) used STO's centered at a single point in the molecular frame. The advantage of the single centre method is that all integrals are easily derived, but more terms are needed for an adequate description of the molecular wave-functions.

Considerable simplification in the evaluation of many center integrals was achieved by using Gaussian and associated functions, called Gaussian-type orbitals (GTO), instead of STO's for the radial parts of the orbitals with retention of spherical harmonics as angular functions. The first systematic consideration of integrals over GTO's is that due to Boys (Ref 50).

Since then several other papers using GTO's have been published (Ref 68). The GTO's are of the form:

\[ \chi(x, y, z) = N \phi(x, y, z) \exp(-\alpha r^2) \]

where \( x, y, z \) are Cartesian coordinates relative to the function's center, \( N \) is the normalization factor. The prefactor \( \phi(x, y, z) \) is 1 for \( s \)-type GTO's; \( x, y, z \) for \( p \)-type GTO's; and \( 3x^2, 3y^2, 3z^2 \) for \( d \)-type GTO's.

A new development in the LCAO-MO-SCF method based on GTO's is the use of contracted Gaussian functions (CGF) and Gaussian lobe functions (GLF) instead of ordinary GTO's. A CGF \( \chi \) represents a linear combination of GTO's:

\[ \chi(x, y, z) = \sum_{q} A_q \phi_q(x, y, z) \]

The set of primitives \( \phi \) in which a particular CGF is expanded are generally constrained to have the same center and to be of the same type. This limitation allows the form of the CGF, defined in (5-63), to simplify to:

\[ \chi(x, y, z) = \sum_{q} A_q \phi_q(x, y, z) \exp(-\alpha_q r^2) \]

Thus a CGF is completely determined by its type, its center, a set
of exponents $\alpha$ and a set of coefficients $A_i$. The coefficients and the exponents may be taken from atomic SCF results, from previous molecular calculations, or from other sources. The coefficients of the contracted functions are again determined variationally.

The use of both GTU's and GCP's give rise to integrals involving products of Gaussian functions with spherical harmonics. In multicenter problems, the use of spherical harmonics introduces computational difficulties.

For this reason GCP's are constructed (Wu 63). A GCP is also a linear combination of simple Gaussian functions of the form $\exp(-r^a)$, without the use of spherical harmonics. The angular dependence in $p$ and $d$-atomic orbitals is achieved by centering the GTU's at different points of space, determined in part by the symmetry of the orbital to be expanded.

The use of both GCP and GCP basis sets turns out to offer attractive possibilities to obtain good approximations to molecular Hartree-Fock solutions with limited basis sets.

Good values for the total energies were obtained for the water molecule by means of LCAO-SCF-MO methods using both STO, GTO, GCP and GCP basis sets (Kar 67, Aum 66, Neu 66). As shown by Mulliken (Mull 66), a satisfactory value for the total energy does not necessarily imply a good description of the charge distribution. For this reason several authors calculated recently one-electron properties of the water molecule. Comparison of the calculated values with experimental results serves as a check in the results of the several types of calculations.

Harrison (Har 67) used GCP in his calculation as basis set, containing four $s$-type and two sets of $p$-type orbitals on the oxygen nucleus and one $s$-type and one set of $p$-type orbitals on the proton. The resulting values for the total energy and for several one-electron properties are given in Table 5-7;

Neuman and Mokowitz (Neu 66) calculated total energy and one-electron properties of the water molecule using both GTU's and GCP's. The GTO set contained ten $s$-type, six sets of $p$-type, and two sets of $d$-type functions centered on the oxygen atom, and four $s$-type and two sets of $p$-type functions centered on the proton. The contracted basis set included five $s$-type, three sets of $p$-type and two sets of $d$-type functions at the oxygen nucleus and two $s$-type and one set of $p$-type functions at the proton. The resulting values for the one-electron properties of interest are also given in Table 5-7.

Aug, Fitzer, and Chan (Aum 68) started from STO's. Their most extensive wave function is based on a basis set of 26 functions: three $s$-type, three sets of $p$-type, and one set of $d$-functions on the oxygen nucleus and two $s$-type and one set of $p$-type functions on the proton. The results are given in Table 5-7. In addition, the authors obtained contour maps of the electron density. In Fig. 5-3 is shown the map in the molecular plane and in Fig. 5-4 in the perpendicular plane bisecting the bond angle. It is seen from these figures that the distribution of the electronic charge is quite symmetrical.

![Contour map of the electron density](image)

**Fig. 5-3.** Contour map of the electron density (in atomic units) in the plane of the water molecule. Only a half plane is shown.

The value of the quadrupole moment of $^{17}$O, adapted in these calculations: $Q = 0.024$ a.u., is that of Bessis et al (Bess 62) obtained from the observed quadrupole constant for the $^3P_z$ state of atomic oxygen and the electric field gradient calculated with configuration.
interaction. For the quadrupole moment of the deuteron we have accepted a value of +0.002796 b (Kur 64).

The experimental values for the several one-electron properties are collected in the last column of Table 5-7. Except for the total energy (Aum 68) and the magnitude of the dipole moment (Bel 57), all these properties have been measured by means of beam-noser Zeeman spectroscopy.

5.6.2 Discussion

There are at least three possible explanations for the existing discrepancies between the calculated one-electron properties of water and the present experimental results:

1) slight differences between the actual geometry of the molecule and the geometry assumed in theoretical calculations,

2) zero-point vibrational effects,

3) unsatisfactory molecular wave function.

Another obvious explanation - unsatisfactory measurements - may be completely disregarded in view of the very high accuracy of the present measurements and the excellent overall fit.

Although the geometries of HDO, D_2O, and H_2O differ slightly, these differences have practically no influence upon the fit of experimental results. Consequently the explanation 1) is a very unlikely one, because differences between the actual and the assumed geometries in the ab-initio calculations are also small.

The second cause for discrepancies - zero point vibrational effects - is recently investigated by Kern and Matcha (Ker 68). They performed averaging of one-electron properties in the lowest vibrational states of the isotopic species of water. Their results were based upon the minimal basis wavefunctions of Reeves and Boys (Boy 56, Boy 57) and the experimental vibrational data of Papousek and Pliva (Pap 64). Each HO was represented by a linear combination of eight STO's. As can be seen from Table 5-7, various one-electron properties obtained by Kern and Matcha, especially the quadrupole coupling tensor at the oxygen nucleus and the molecular quadrupole tensor, differ significantly from other theoretical and experimental values. This may be due both to the limited number of basis functions and to inaccuracies in the calculation of multiconfigurational integrals. Although the wave functions of Reeves and Boys are less accurate than the other mentioned wave functions, their results are listed in Table 5-7 because they represent the order of magnitude of vibrational corrections. As can be seen in Table 5-7, the vibrational corrections are typically about 1%, but can be as large as 10%.

For this reason the performance of the several wave functions used in the calculation of the one-electron properties is investigated by comparing the calculated and experimental values of the one-electron properties, taking into account vibrational effects.

It is seen from Table 5-7 that agreement between the theoretical calculations of the quadrupole coupling by various authors and the experimental value is very good for the deuteron side, usually better than to within 10%, in spite of the fact that the electronic and nuclear contributions are of opposite sign (see below). This is also the case for the asymmetry parameter $n(0)$, but the agreement is somewhat misleading in this case. Although most comparison between theory and experiment were keyed in the past on $n$ because of its independence on the exact value of the nuclear quadrupole moment, this parameter is
<table>
<thead>
<tr>
<th>Units</th>
<th>7-dependence</th>
<th>Theoretical values</th>
<th>Experimental values</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Kern and Matcha</td>
<td>Harrison</td>
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<td></td>
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<td>(Ker 68)</td>
<td>(Har 67)</td>
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<td></td>
<td>STD's a)</td>
<td>STD's b)</td>
<td>GDF's</td>
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<td>Total energy a)</td>
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<td>$-75.766$</td>
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<td>$0.72$</td>
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<td>$\left(\frac{\partial}{\partial z}^2\right)$ (0)</td>
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<tr>
<td>$\eta (0)$ (a)</td>
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<td>$10^{-6}$</td>
</tr>
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</table>

Table 5-7. Theoretical and experimental values of one-electron properties and the total energy of the water molecule. The symbol 'v' indicates that the experimental values are obtained in the present work.

a) Without correction for zero point vibrations.
b) Including correction for zero point vibrations.
c) All values are without the extra correlation energy and relativistic correction.
d) As quoted by Aung et al (Aum 68).
e) $x', y', z'$ represent the principal axes system of the electric quadrupole coupling tensor at the deuteron in D$_2$O; see Fig. 5-1.
f) $n (D) = (\eta (D) - \eta (H)) / (\eta (D) - \eta (H))$
g) $\phi$ is the angle between the 0-D bond and the principal $z'$-axis; see Fig. 5-1.
h) The sign of the dipole moment is obtained in this work.
i) The $x, y, z$ axes system is identical with the $(c,a,b)$ axes system; see Fig. 5-1.
not a sensitive test of a calculation. It is evident from the definition of $\eta$, that errors in the components of the quadrupole coupling tensor can cancel out to a large extent. A clear example of this cancellation is seen in the results of Kern and Hatcha. Although their value of $\eta$ agrees well with the present experiments, the results for the tensor elements of $^{17}$O disagree by a factor of almost two. As we do not know any details of the used wave functions it is hard to say which features (e.g., insufficient flexibility of the oxygen orbitals) are responsible for the large discrepancy.

Agreement between the calculated values of the components of the quadrupole coupling tensor of $^{17}$O by Harrison, by Aung et al., and by Neu mann and Moskowitz is not as good as at the deuteron, but none the less surprisingly good ($5 \pm 20 \%)$, taking into account the complicated nature of the calculations. Explicit calculations of Neu mann and Moskowitz indicate that the nuclear and the total electronic contributions to the quadrupole coupling at the deuteron are nearly equal but opposite in sign; the molecular orbitals $3a_1$, $2a_1$, $3b_1$, $1b_2$, and $1b_1$ contribute roughly equally to the electric gradient. This indicates that the deuteron coupling constant is determined only by the gross features of electronic distribution, and, consequently, is less sensitive to the detailed shape of molecular orbitals.

The situation is entirely different at the oxygen nucleus. The nuclear and the total electronic distribution have the same sign (+), and the latter contribution is determined almost completely by the outer orbitals $3a_1$, $1b_2$, and $1b_1$, with a rather clear predominance of $1b_2$ for the $xx$-element and of $3a_1$ for the $zz$-component.

As the outer orbitals are much more sensitive to the choice of the basis set than the inner ones and are, in consequence, less accurately known, the somewhat poorer agreement for $^{17}$O is not surprising.

In the case of $^{16}$O the vibrational corrections to the equilibrium values of the deuteron field gradients are found to be about one per cent. This is an order of magnitude less than the discrepancies between calculated and experimental values. The vibrational corrections for the oxygen field gradient are about one per cent for the $xx$ and $yy$ components and about 10 % for the $zz$ component. Assuming that the same corrections have to be applied also to the oxygen field gradient as calculated by Neu mann and Moskowitz and by Aung et al., the agreement between the calculated and experimental values improves considerably.

The excellent agreement (see Table 5-7) between the calculated and the experimental values for the average magnetic shielding at the proton is not surprising. The $T^{-1}$ operator plays an important role in the Hamiltonian and is therefore favored in the variational method for the energy.

Due to the higher nuclear charge, the operator $T^{-1}$ plays an even more important role in the Hamiltonian and its expectation value can therefore be expected to be also reasonably accurate. This explains also the large similarities between the values for $T^{-1}$ as calculated by several authors (see Table 5-7). We may conclude from the foregoing that reasonably accurate values for the anisotropies in the diamagnetic shielding tensor of the deuteron may be obtained from the several basis sets. These anisotropies can then be compared with the measured anisotropies in the total magnetic shielding as discussed in Sect. 5.5.

With the exception of the less accurate calculations of Kern and Hatcha, all other recent ab-initio calculations yield electric dipole moments which are slightly larger than the experimental value. The difference is larger than the vibrational correction. Detailed calculations by Neu mann and Moskowitz show that the addition of $\pi$ and $\delta$-type orbitals results in a distortion of the charge distribution, which has large effect on the shape of the $3a_1$ and $1b_2$ orbitals and their contributions to the dipole moment. According to Mulliken's views a limited configuration interaction will also decrease the magnitude of the calculated dipole moment (Mul 62).

The calculated values of the isotropic part of the charge distribution $\langle F_1 | F_1 \rangle^{(2)}_E >$ are all in good agreement with the experimental result. The operator $\langle F_1 | F_1 \rangle^{(2)}_E >$ seems to be a rather insensitive test of the shape of the wave function. The fact that all calculated values of $\langle F_1 | F_1 \rangle^{(2)}_E >$ are slightly larger than the experimental values indicates that the true wave function is probably more contracted because of the correlation effects than any of the applied approximations might suggest.

The operator $\langle 6s^2 | 4s \rangle_{av}$ is proportional to $\langle F_1 | F_1 \rangle^{(2)}_E - \langle F_1 | F_1 \rangle^{(2)}_P >$.
and represents a measure of the shape, or the deviation of the electronic charge distribution from spherical symmetry. The molecular quadrupole moment represents a similar quantity but includes also the nuclear charges.

Taking into account the complicated nature of the calculations, the agreement between the calculated and experimental values for \( Q_{zz} \) and \( Q_{xx} \) is rather good. Kern and Matcha reported zero-point vibrational correction only for the molecular quadrupole moment and not separately for the nuclear and the electronic contributions. Their calculations indicate that, generally, the vibrational correction does not remove discrepancy between computed and experimental values of the quadrupole moment. Neumann and Moskowitz (Neu 68) and Aung et al. (Aun 68) have calculated the nuclear contribution to the molecular quadrupole moment for a number of geometries of \( H_2O \). The results suggest a strong dependence of the nuclear part of \( Q_{zz} \) on the molecular geometry and by consequence partial cancellation of the vibrational corrections to the electronic and nuclear contributions.

The electronic model proposed by Harrison shows that \( \frac{1}{2} \left\langle \frac{1}{2} \vert \mathbf{J} \vert \left\langle \frac{1}{2} \right\rangle \right. \) is too large and \( \frac{1}{2} \left\langle \frac{1}{2} \vert \mathbf{L} \vert \left\langle \frac{1}{2} \right\rangle \right. \) too small compared with the measured values. Apparently the outer electrons are more contracted to the x-axis and less to the z-axis than in the model of Harrison. On the other hand the outer electrons in the model of Aung et al. are too much contracted in the plane of the molecule. The models of Neumann and Moskowitz show a too high concentration at the \( x \)-axis at the cost of the concentration at the \( x \)-axis. These discrepancies may be due both to vibrational effects and to a limited basis set used in the calculation of the electronic charge distribution.

5.7 CONCLUSIONS

The good agreement between the present experimental results and the calculations of Harrison, Aung et al., and Neumann and Moskowitz is significant for several reasons. It shows that reliable ab-initio calculations of molecular properties are feasible and that essentially the same results can be obtained with a limited basis of multiconfigurational

GIF's, GTO's, GTO's, and with GIF's. All calculations give better results at the deuteron than at the oxygen nucleus for the quadrupole interaction, indicating deficiencies of outer less tightly bound orbitals which may also cause the discrepancies found for the diamagnetic susceptibilities and the molecular quadrupole moment.

At this stage of comparison of accurate calculations and high-accuracy experiments, one must abandon the expressions derived in the rigid rotor model and take into account zero point vibrational effects. As discussed in this work, the rigid rotor expressions for the magnetic moment and for the magnetic susceptibility tensor may well be affected by isotopic substitution, especially in their paramagnetic parts.

A similar behavior may also be expected for hyperfine interaction tensors. This may explain the discrepancies between the hyperfine constants of several rotational levels of \( HDO \) and \( D_2O \), as reported in Sect. 4.2.1.

However, the electronic distribution as proposed by Harrison, by Aung et al., and by Neumann and Moskowitz, represents the results of the experiments fairly well without a clear preference for one of these calculations.

In order to serve as a further test of the electronic wave functions, it is desirable that future calculations also include the anisotropies in the diamagnetic shielding.

Further investigation of the centrifugal and vibrational effects may be performed in future by measuring magnetic and hyperfine coupling constants of other levels of isotopic species of water. The interaction tensors may then be determined for each isotopic species separately. Comparison of each interaction tensor between the isotopic species may give detailed information on the centrifugal and vibrational effects.

The present results for the quadrupole coupling constants, spin-rotation coupling constants, the sign of the electric dipole moment, the molecular quadrupole moment, the molecular magnetic moment, and the magnetic susceptibility show that the beam-maser Zeeman spectrometer is a powerful tool in obtaining these data. The present experimental results and the recent reliable GIF calculations make water, next to hydrogen, the most thoroughly investigated molecule.
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SAMENVATTING

In dit proefschrift worden experimentele waarden voor verschillende 66-creating eigenschappen van het watermolecul, die tot nu toe niet of zeer onnauwkeurig gemeten waren, bepaald en vergeleken met recente ab-initio berekeningen voor de grondtoestand van het watermolecul.

Een oversicht van de elektronische eigenschappen, die alleen afhankelijk van de elektronische grondtoestand, is gegeven in hoofdstuk 1. De belangrijkste zijn: het elektrisch dipoolmoment, de quadrupoolmoment, de gradiënt van het elektrisch veld ter plaatse van het proton en van het zuurstofkern, de diamagnetische afwijking van de kern, en de diamagnetische susceptibiliteit. Van deze grootheden waren tot nu toe alleen de absolute waarde van het dipoolmoment en de gradiënt van het elektrisch veld ter plaatse van het proton goed bekend. Waarden voor de resterende grootheden worden in dit proefschrift bepaald uit het Zeeman-effect en de hyperfijnstructuur van de rotatie-overschering van isoeto watermoleculen. Deze effecten zijn gemeten met een beam-meeter Zeeman-spectrometer.

Deze mikrogeolf-spectrometer is gebouwd (zie hoofdstuk 2) naar een voorbeeld van Thaddeus en Dreischer (1961) en van Blyusen (1968). Hiermee verschilt de huidige spectrometer echter voornamelijk door de aanwezigheid van een stabiel en homogen magnetisch veld in de trihalite. Ter vergroting van de gevoeligheid is er verder een systeem ontwikkeld om "time-averaging" technieken toe te passen. Met deze spectrometer zijn Zeeman-overscheringen van ongeveer 5 MHz, met een lintbreedte van 2 KHz, gemeten bij een magnetieke veld van 12 KG.

Interpretatie van de gemeten Zeeman- en hyperfijn-spectra is gebaseerd op de Hamiltoniaan die behandelde in hoofdstuk 3. Met behulp van sferische operatortechinen zijn de Zeeman- en hyperfijn-overscheringen berekend in termen van een aantal koppelingsconstanten. De invloed van tweede-orde effecten op de spectra is onderzocht.

De meetresultaten worden besproken in hoofdstuk 4. De metingen van de hyperfijnstructuur van de $^2P_1$-overgang van $^{16}O$ geven nauwkeurige waarden voor de gradiënt van het elektrische veld ter plaatse van de zuurstofkern. De resultaten van de hyperfijn-overschering van de $^1S_0$ overgang van $^{18}O$, van de $^1D_2$ en $^3P_2$ overgang van $^{2}D_2$, en van de $^3P_1$, $^1D_2$ overgang van $^{2}D_1$ zijn van belang om de invloed van centrifugale distorsie en isotope effecten op het starrer-rotor-model te onderzoeken. Het blijkt dat de bovengenoemde effecten veelbreder bijdragen hebben. Het Zeeman-effect van de $^2P_1$ overgang van $^{16}O$, van de $^3P_2$ en $^3P_1$ overgangen van $^{2}D_2$, en van de $^3P_1$, $^1D_2$ overgang van $^{2}D_1$ is gemeten. De moleculaire magnetische momenten zijn bepaald tot ongeveer 0.05% nauwkeurig en de koppelingsconstanten voor de magnetische susceptibiliteit tot ongeveer 10%. Bijdragen van de magnetische afwijking van de kern zijn erg klein en hebben een relatief grote onnauwkeurigheid.

De gemeten koppelingsconstanten zijn geanalyseerd in hoofdstuk 5 en zijn daar vergeleken met ab-initio berekeningen. De gradiënt van het elektrisch veld ter plaatse van de zuurstofkerns toont grote verschillen met eerder gemaakte meetingen, maar is in goede overeenstemming met ab-initio berekeningen. De moleculaire magnetische momenten van de deels van $^{16}O$ worden geen bijdrage van de centrifugale distorsie. Vergelijking met de waarden van de moleculaire magnetische momenten van $^{18}O$ geeft voor het dipoolmoment een waarde, die 205% afwijkt van de waarde die volgt uit meetingen van het Stark-effect van water. Het blijkt dat deze discrepantie veroorzaakt wordt door nullpoint-vibratie-effecten. De waarden voor de koppelingsconstanten van de magnetische susceptibiliteit en van de moleculaire magnetische momenten zijn verschillende 66-creating eigenschappen bepaald: o.a. het moleculaire quadrupoolmoment.

Deze experimenteel bepaalde waarden van 66-creating eigenschappen voor de grondtoestand van water verkennen van goede overeenstemming met ab-initio berekeningen (Tabel 5-7). Dit betekent dat betrouwbare ab-initio berekeningen van de betreffende grootheden mogelijk zijn. Het blijkt dat dezelfde resultaten kunnen worden verkregen met een beperkte basis van zowel meer-crenta QMP's, OTP's, STO's, en OP's.
pulps trillingen van het molekuil bij het vergelijken van de zeer nauwkeurige meetresultaten met waarden voor één-elektron eigenschappen zoals die op dit moment berekend kunnen worden.

Aan het einde gekomen van dit proefschrift wil ik graag al diegenen bedanken, die op enigerlei wijze een aandeel gehad hebben in het tot stand komen van dit werk. Enkel van hen wil ik in het bijzonder dankbaar vermelden.

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