

III. ATOMIC RESONANCE AND SCATTERING*

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RESEARCH OBJECTIVES AND SUMMARY OF RESEARCH

Our interests center on the structure and interactions of atoms and simple molecules, and on their interactions with radiation at both optical and radio frequencies. Experimental methods involve colliding beam scattering, atomic and molecular beam resonance spectroscopy, high precision maser spectroscopy on stored atoms, and optical fluorescence with tunable lasers.

1. Van der Waals Molecules

Van der Waals molecules are held together by long-range interatomic forces, in contrast to the chemical forces which hold together normal molecules. Because these forces are roughly 100 times weaker than chemical forces, van der Waals molecules are frail and difficult to observe. We have produced a molecular beam of isolated, paramagnetic van der Waals molecules and are executing measurements on their optical and magnetic properties.

2. Atomic Scattering Studies

We are continuing our studies of atomic scattering using polarized atomic beams. We have recently installed a new source which improves our intensity substantially, and permits us to extend our studies to collisions that form complexes. Work is under way toward the use of a tunable dye laser to produce a beam of excited-state atoms for use in our collision studies.

3. High Precision Studies with the Hydrogen Maser

We are nearing completion of a program to measure the magnetic moments of hydrogen and deuterium to very high precision. The results bear on the fundamental theory of magnetic interaction in simple atoms, and are of use in evaluating fundamental constants. During the past year we have completed a measurement of the magnetic moment of the deuteron in terms of the Bohr magneton.

4. Interactions in the Excited State

We have initiated a program to measure atomic interactions in the excited state. Our first efforts were directed toward creation of an optically excited diatomic complex. We

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believe that we have evidence for the complexes. The results are of interest in the theory of superradiance, and also because they demonstrate a previously unobserved reaction process – the formation of a molecule from the continuum at low pressure through absorption of a photon.

D. Kleppner, D. E. Pritchard

A. VAN DER WAALS MOLECULES

Joint Services Electronics Programs (Contract DAAB07-71-C-0300)
NSF (Grant GP-28679)

E. M. Mattison, J. Apt III, D. E. Pritchard, D. Kleppner

A molecular-beam apparatus has been constructed for studying the magnetic-resonance spectrum of van der Waals molecules. The design philosophy of the machine was described in a previous report.¹ A diagram of the apparatus is shown in Fig. III-1. The source chamber is constructed from a stainless-steel cross of tubing of 12 in. diameter. It is pumped by an unbaffled 10-in. diffusion pump that has a speed of 4200 liters/second, which is adequate for handling noncondensable gases from the jet source.

The entire source apparatus, including oven and skimmer, is suspended on a carriage that rotates about a point in the first deflecting magnet. The spin state is selected by moving the carriage. The oven's body, top and nozzle are equipped with independent heaters and thermocouples. The height and direction of the oven, the lateral position of the skimmer, and the distance between the skimmer and nozzle, can each be controlled. A collimating chamber, downstream from the source chamber, provides differential pumping by means of a 600 liters/second diffusion pump.

After leaving the collimating chamber, the beam passes through the magnet chamber.

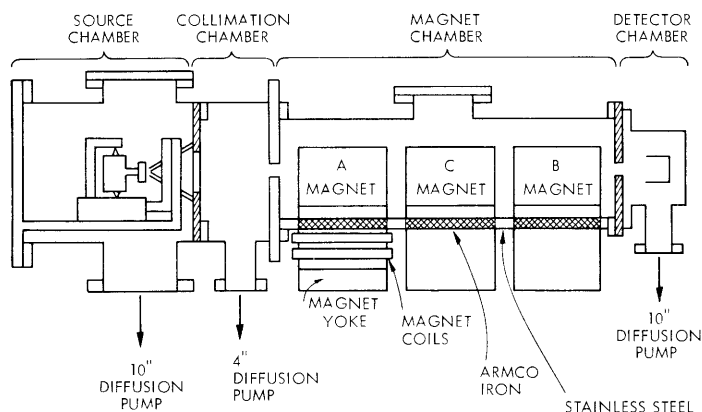


Fig. III-1. Molecular-beam apparatus for studying van der Waals molecules.

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This chamber, which is fabricated from stainless-steel tubing, has a flat floor with magnetic steel inserts to conduct the flux of the deflecting and homogeneous magnets. This arrangement allows the magnet coils to be external to the vacuum.

The detector housing is attached to the exit of the magnet chamber, and is pumped by a Vac-ion pump. The detector includes a hot-wire surface ionizer, a mass spectrometer, and an electron multiplier. The detector has a maximum count rate of 10^6 counts per second and a measured overall detection efficiency of approximately 0.3.

We have produced beams of potassium atoms, with the oven operated as an effusive source, and have observed transitions between the Zeeman levels of the upper hyperfine state. The width of this resonance, approximately 40 kHz, agrees with that calculated from the resonance coil length and estimated beam velocity.

Work is in progress to produce a potassium-argon beam.

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B. MAGNETIC MOMENT OF THE DEUTERON

Joint Services Electronics Programs (Contract DAAB07-71-C-0300)
NBS (Grant NBS2-9011)

W. D. Phillips, W. B. Cooke, D. Kleppner

Existing high-precision measurements of the deuteron magnetic moment have been performed by means of nuclear magnetic resonance (NMR) with molecular samples.¹⁻³ The proton and deuteron NMR frequencies are compared in samples such as H₂O and D₂O, H₂ and D₂, and HD. In all but HD the proton and deuteron are in different molecular environments, and therefore have different diamagnetic shieldings. Even in HD, the shielding for the two atoms in the molecules is not exactly the same. Since the differences in shielding are of theoretical interest, it is important to have a measurement of the deuteron moment that is independent of any molecular environment. We have made preliminary measurements of the deuteron/electron magnetic-moment ratio in atomic deuterium with a high-field deuterium maser. We expect the final precision of our measurement to be $1-2 \times 10^{-8}$ compared with 5×10^{-8} for the best molecular measurements.² We use a method similar to that of Winkler et al.⁴ for the measurement of the proton/electron moment ratio.

1. Theory

The energy levels of ground-state deuterium in a magnetic field are shown in Fig. III-2, where m_j and m_I refer to the projections of the electron and nuclear spins on the direction of the magnetic field.

The energy level in Fig. III-2 given by the Breit-Rabi formula for deuterium is

$$\frac{E(m, m_j)}{h} = \frac{-\nu_0}{6} - m\nu_J R \pm \frac{\nu_J}{2} (1+R) \left\{ 1 + \frac{4m}{3} \frac{\nu_0}{\nu_J(1+R)} + \frac{\nu_0^2}{\nu_J^2(1+R)^2} \right\}^{1/2}, \quad (1)$$

where ν_0 is the hyperfine separation, $\nu_J = -g_J\mu_0 H/h$ is the field-coupled electron spin flip energy, $R = g_I/g_J$, and \pm refers to the sign of m_j .

By means of microwave- and radio-frequency double resonance, the frequencies of the transition $2 \rightarrow 5$ and one of the transitions a, b, c, and d are measured simultaneously. These two frequencies can be used with Eq. 1 to give the moment ratio R. Since corrections to free space of atomic moments are calculable for hydrogenic atoms,⁵ this leads to the deuteron moment in Bohr magnetons.

There are several systematic errors which can affect the measurement of the moment ratio: Collisions between deuterium atoms during the measurement process cause frequency shifts attributable to spin exchange. Collisions of the atoms with the

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walls of the storage bulb cause a shift in the hyperfine frequency. Asymmetric distributions of magnetic-field inhomogeneities cause a shift in the observed frequency from that expected on the basis of the average magnetic field. If the microwave cavity into

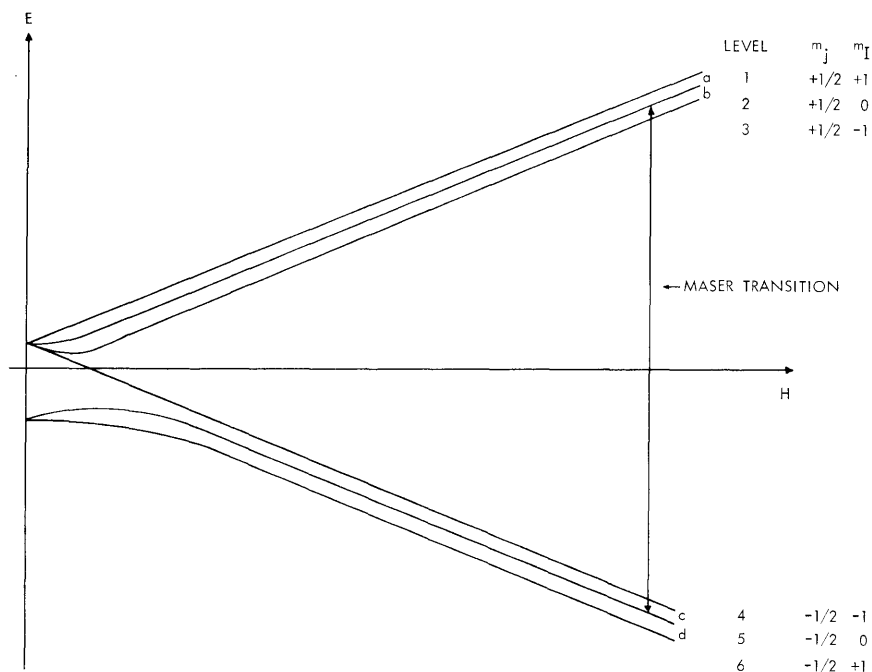


Fig. III-2. Energy levels of deuterium in the ground state.

which the deuterium atoms radiate when they undergo an electron spin flip is not tuned to the spin-flip frequency, there will be a cavity pulling of the frequency. Similarly, if the circuit that drives the nuclear spin flip is not tuned to the nuclear frequency, there will be a shift.

Fortunately, the error in the moment ratio produced by most of these effects changes sign when a different nuclear transition is used. For example, when the cavity pulling causes a positive shift for transitions a and c, it is negative for b and d. Because the frequency of each nuclear transition is different, pulling caused by mistuning of the circuit driving these transitions does not reverse sign in a simple way. This effect, however, can be made quite small. For all the other effects, the theoretical expectation is that averaging the results for all four possible nuclear transitions should result in a value for the moment ratio free of the systematic effects described, except for a small fraction of the wall shift, which can be corrected for.

2. Experiment

The experimental procedure for this measurement is basically that used by Winkler et al.⁴ in their measurement of the proton moment. It was necessary, however, to make

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a substantial improvement over the absolute precision that they achieved in order to obtain the same relative precision. This is because the field-coupled part of the nuclear transition frequency is approximately 7 times smaller for deuterium than for hydrogen. The linewidth, however, is the same. Thus to achieve the same 1×10^{-8} precision in the deuteron moment as was obtained for the proton moment, 7 times greater absolute precision in the transition frequency is required.

The major limitation on the measurement of Winkler et al. was the inhomogeneity shift. By greatly reducing the magnitude of this shift and using different transitions to cancel the remaining shifts, we have been able to approach the desired precision.

The inhomogeneity shift in the proton moment experiment was caused by a rather large collimator on the neck of the maser storage bulb. The collimator was made of Teflon tubes and constituted $\sim 3\%$ of the bulb volume. By using glass collimators that occupy only 0.1% of the bulb volume, we have greatly reduced the inhomogeneity shift.

3. Results

The result of measurements taken thus far is

$$g_I/g_J = 2.332172696 \times 10^{-4}.$$

This result is uncorrected for systematic effects and represents simple averaging of measurements on all four nuclear transitions. The statistical uncertainty is less than 1×10^{-8} . The question of uncertainty attributable to systematic errors is under consideration. Tests with different sized collimators have shown no inhomogeneity shift. Results of spin-exchange measurements made by varying the density of atoms in the storage bulb show no effect, in agreement with theory, but the tests are only accurate to 3×10^{-8} because of the poor signal-to-noise ratio obtained at the low density that they require. We are currently studying the wall shift. Cavity pulling has been shown to behave as expected theoretically and should cause no error when all transitions are averaged. The effects of mistuning the nuclear frequency circuits have been calculated to be negligible.

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C. DIAMAGNETIC SHIELDING OF H₂

Joint Services Electronics Programs (Contract DAAB07-71-C-0300)
NBS (Grant NBS2-9011)

A. G. Jacobson, W. D. Phillips, D. Kleppner

1. Introduction and Background

The diamagnetic shielding constant for the proton in molecular hydrogen, $\sigma(\text{H}_2)$, has received extensive theoretical study, and is the most likely candidate for ab initio calculation. As part of an effort to obtain a precise absolute experimental value for $\sigma(\text{H}_2)$, we have compared the NMR frequency of protons in H_2 and in tetramethylsilane, $(\text{CH}_3)_4\text{Si}$, a popular NMR standard. A companion experiment to compare the proton frequency in tetramethylsilane (TMS) and in atomic hydrogen is under way in our laboratory. The diamagnetic corrections in hydrogen are known with great precision and the two experiments will be combined to yield an absolute value for $\sigma(\text{H}_2)$.

The shielding constant σ is related to the observed NMR frequency ν by

$$\nu = (1-\sigma)(\gamma/2\pi)\langle B \rangle, \quad (1)$$

where γ is the gyromagnetic ratio of the free proton, and $\langle B \rangle$, the average magnetic field at the site of the proton, is related to the applied field B_0 by

$$\langle B \rangle = B_0(1-g\chi), \quad (2)$$

where χ is the bulk susceptibility, and g is a geometrical factor. Under the assumption that the two samples have the same geometry, Eqs. 1 and 2 give, to a good approximation,

$$\sigma(\text{H}_2) - \sigma(\text{TMS}) = 1 - \frac{\nu(\text{H}_2)}{\nu(\text{TMS})} - g[\chi(\text{H}_2) - \chi(\text{TMS})]. \quad (3)$$

The average and applied fields differ because of the depolarizing effect of the sample, and the effect of nearby dipoles. Under the assumption that the nuclear motion is perfectly random so that the molecule effectively "scoops out" a spherical Lorentz cavity, the nearby dipoles produce a local field

$$B_{\text{loc}} = \frac{4\pi}{3} M = \frac{4\pi}{3} \chi \langle B \rangle.$$

The bulk polarizability produces a demagnetizing field

$$B_{\text{demag}} = -x\chi B_0,$$

where x is a factor dependent on the sample geometry. If we use $\langle B \rangle = B_0 + B_{\text{loc}} + B_{\text{demag}}$,

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it follows that

$$g = x - 4\pi/3, \tag{4}$$

where we have assumed that $g\chi \ll 1$.

For a spherical sample, $x = 4\pi/3$ and $g = 0$. The samples used were cylindrical, however, and in this case $x = 2\pi$ and $g = 2\pi/3$.

3. Method

a. Sample Preparation

The TMS and hydrogen samples were contained in identical heavy wall NMR tubes, 5 mm OD, 2.12 mm ID (Wilmad, Type 522-PP). Matheson research grade hydrogen was used in a sealed sample at a pressure of 30 atm. The TMS, supplied by the Thompson-Packard Corporation, was outgassed by repeated cycles of freezing and evacuation.

b. Spectrometer

The measurements were made with a 60-MHz Hitachi-Perkin-Elmer R20B NMR spectrometer. The TMS sample, but not the hydrogen sample, was spun. Under optimal conditions the TMS linewidth was 0.6 Hz and the H_2 linewidth was 100 Hz. The magnetic field was stabilized by an independent NMR field-locking system.

c. Procedure

In the experiment we successively observed the TMS and the hydrogen resonance signals. The TMS frequency was determined by displaying the resonance on a recorder, and calibrating the frequency at several points on the curve. Because of the high signal-to-noise ratio and narrow linewidth, the TMS resonance frequency could be identified essentially to 0.1 Hz by inspection.

The hydrogen resonance frequency was determined by slowly sweeping the spectrometer frequency and digitally recording the resonance signal and spectrometer frequency. Typically, 40 points were taken during a frequency sweep of 300 Hz. A single sweep took 400 s, and the system time constant was 5 s. The line was swept successively in opposite directions to eliminate distortion from the finite sweep speed. The data were fitted to a five-parameter Lorentzian absorption-dispersion curve.

d. Verification of Shielding Correction

We made an effort to verify the value of the product $g\chi(\text{TMS})$, where g is the geometrical factor, which we took to be exactly $2\pi/3$, (the value for an infinite cylinder) in our data reduction. By using this value with the Frei and Bernstein¹ result for $\chi(\text{TMS})$, we predicted a difference of 68.2 Hz between the NMR frequencies of cylindrical and

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spherical samples of TMS at 60 MHz. Our spherical samples were 4-mm spheres fitted with thin cylindrical filling stems. The spheres were held by their stems in an ordinary thin-walled 5-mm NMR tube by Teflon chucks. They were compared with a variety of cylindrical TMS samples, including the one used in the H_2 measurements.

The results were inconclusive, because of unpredictable broadening, asymmetry, and spikes in the resonance line shape from the spheres. The difficulty may have been caused by paramagnetic impurities or magnetic field inhomogeneity. In a few measurements in which the resonance lines were narrow and symmetrical, we obtained the results 57.5, 62.0, and 63.2 Hz, in comparison with the predicted value of 68.2 Hz. Thus, although these results were consistent with the predicted result, they are not definitive.

3. Results

Final results were based on a series of 19 independent determinations taken over a period of 10 weeks. The raw data are shown in Fig. III-3. They represent the absolute

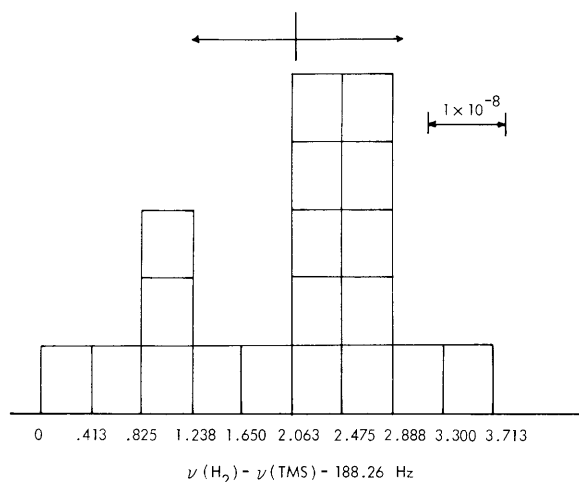


Fig. III-3. Experimental results for comparison of the NMR frequencies of the proton in H_2 and TMS.

difference between the H_2 and TMS samples. For $\nu(\text{TMS}) = 60.000$ MHz, we find, for cylindrical samples,

$$\nu(H_2) - \nu(\text{TMS}) = 190.32(83) \text{ Hz},$$

where the uncertainty represents one standard deviation. To obtain $\sigma(H_2) - \sigma(\text{TMS})$, we use Eq. 3 with $g = 2\pi/3$ and the following values for susceptibility:

$$\chi(\text{TMS}) = -0.543(5) \times 10^{-6}$$

$$\chi(H_2) = -4.89(49) \times 10^{-9}.$$

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$\chi(\text{TMS})$ is from Frei and Bernstein,¹ and $\chi(\text{H}_2)$ is based on a molar susceptibility of $-3.98(4) \times 10^{-6}$ /gram formula weight.² The final result is

$$\sigma(\text{H}_2) - \sigma(\text{TMS}) = -4.299(14) \times 10^{-6}.$$

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D. INTERACTIONS IN THE EXCITED STATE

USAF-OSR (Contract F44620-72-C-0057)

C. Wieman, M. G. Littman, D. Kleppner

We are studying the process $\text{Na} + \overset{\circ}{\text{Na}} + h\nu \longleftrightarrow (\text{NaNa})^*$. The complex $(\text{NaNa})^*$ exists in a coherent superposition of the ground and excited states. The complex is bound by a small first-order dipole interaction energy. The system represents a pure Dicke superradiant state, and for the electronically symmetric state it should have a radiative lifetime exactly one-half that of an isolated excited atom. In our experiment the $(\text{NaNa})^*$ complex is observed indirectly by measuring its fluorescent lifetime.

The superradiant complexes are formed by bombarding sodium in a vapor cell with photons from a pulsed (5-ns) dye laser. The incident photons are at 5950 \AA , well to the red of the D-line transitions (5890 \AA , 5896 \AA). The fluorescent lifetime is measured by standard timing methods. The decay photons are observed through a monochromator with a $5955\text{-}5995 \text{ \AA}$ bandwidth. The binding energy for the complex is approximately 0.02 eV. Fluorescence was observed with a lifetime of 8 ns. The free atom lifetime is 16 ns (we verified this as a calibration check), so that the observed fluorescence is consistent with the formation of the superradiant complexes. We are repeating the experiment to obtain better precision, and to measure the fluorescence spectrum, as well as to study the dependence of the formation rate on the energy of the incident photons.

Work is under way toward refining the measurement and determining both the emission and absorption spectra of the complexes.