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[a] Present address: National Bureau of Standards, Washington, D. C. 20234.

[b] Present address: Department of Chemistry, Carthage College, Kenosha, Wisc. 53141.

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Double-Quantum Saturation Spectroscopy in Hydrogen: Measurement of the $3P_{3/2}$-$3D_{3/2}$ Lamb Shift

E. W. Weber[a] and J. E. M. Goldsmith
Department of Physics, Stanford University, Stanford, California 94305

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Very narrow saturated double-quantum transitions (2^2S-3^2S, 3^2D) have been observed for atomic H in a He-H_2 dc discharge using rf and a cw dye laser. The H $3P_{3/2}$-$3D_{3/2}$ Lamb shift has been measured directly by comparing single- and double-quantum saturation signals to be $-5.5(0.9)$ MHz, confirming that $3D_{3/2}$ lies lower than the $3P_{3/2}$ state. Further applications of the method are discussed.

Saturation spectroscopy[1,2] in hydrogen using single-photon transitions is limited in resolution by the natural lifetime of the broad resonant P levels. Double-quantum transitions between the longer-lived ^2S or ^2D levels, however, will in principle be narrower by more than one order of magnitude, e.g., by a factor of 30 for 2^2S-3^2S compared to the intermediate 2^2S-3^2P transitions, as has been pointed out several years ago.[3] More general theoretical analyses of saturated double-quantum transitions using lasers had been worked out even earlier.[4]

We have demonstrated the feasibility of Doppler-free double-quantum saturation spectroscopy (DQS) of atomic hydrogen using saturated, polarized absorption[2] for the optical transitions 2^2S-n^2P, $n \geq 3$, and a simultaneous rf or microwave transition [n^2P-n^2S ($-n^2D$)]. This method is a practicable alternative to the not yet accomplished possibility of infrared two-photon spectroscopy of excited ^2S (^2D) hydrogenic states. It has the advantage that very low laser intensities (e.g., <20 mW/cm^2 for H$_\alpha$ D_1, $2S_{1/2}$-$3P_{1/2}$) are sufficient to saturate the optical transition. With the high absorption attainable in the He-H_2 dc discharge, the double-quantum transitions can readily be observed with the convenient detection method of saturation or polarization spectroscopy, i.e., as a change in the transmitted laser–probe-beam intensity or polarization. Narrow transitions have also been observed in hydrogen with a purely radio-frequency double-quantum method resulting in a precise determination of the $3S_{1/2}$-$3D_{5/2}$ separation.[5]

The experimental setup is shown in Fig. 1. A single-mode cw dye laser (Coherent Inc. Model 599, Rhodamine 101 dye) pumped by the 568.2-nm line of a Kr$^+$ laser (Spectra-Physics Model 171) provides 50 mW at H$_\alpha$, $\lambda = 656.3$ nm, with a bandwidth of about 1 MHz. A wide discharge tube (5.5 cm i.d.) without wall coating filled with a He-H_2 (1 to 15%) mixture is used to generate the metastable H*(2s) atoms. It has several advantages compared to a conventional narrow (1-cm-diam) Wood's discharge tube with pure H_2 and a wall coating of P_2O_5 and H_2O. The H$_\alpha$ polarization signals are of similar strength for discharge current densities lower by more than a factor of 3. With currents of 50 to 500 mA provided by a hot cathode, H*(2s) densities of 10^9/

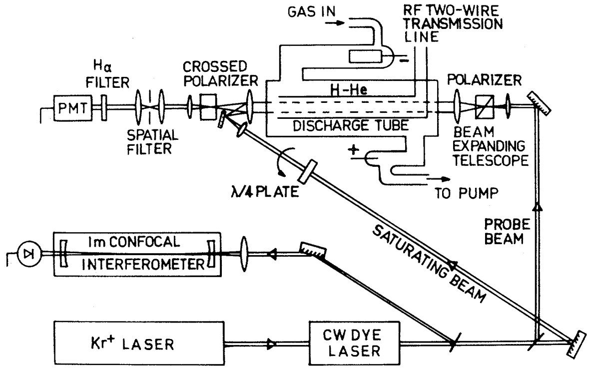

FIG. 1. Experimental setup for double-quantum saturation spectroscopy of atomic hydrogen in a He-H_2 dc discharge.

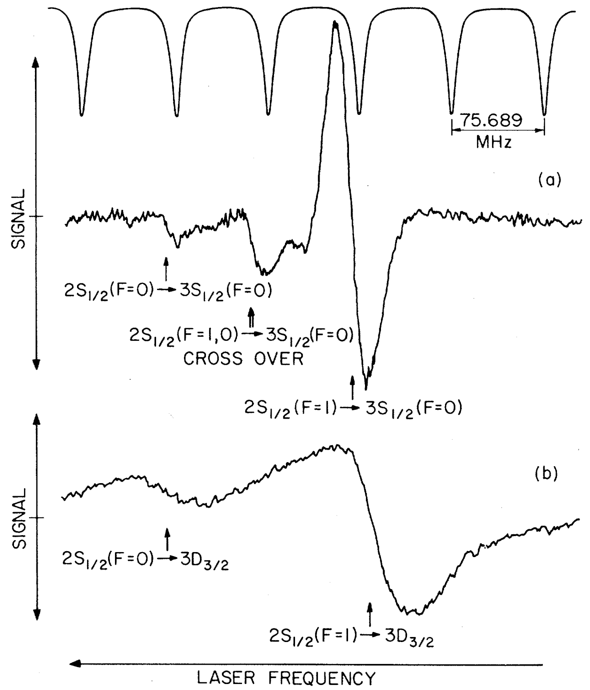

FIG. 2. Saturated double-quantum transitions in atomic hydrogen (a) $2S_{1/2}$-$3S_{1/2}$ and (b) $2S_{1/2}$-$3D_{3/2}$ obtained with polarization spectroscopy and amplitude modulation of the rf. The experimental conditions are (a) $\nu_{rf}=271$ MHz, $p_{\text{He, H}}=0.06$ Torr, discharge current 200 mA; (b) $\nu_{rf}=12.3$ MHz, and data in Table I.

cm^3 up to $10^{12}/cm^3$ are obtained. The axial electric field in the positive column measured with two probe electrodes 14 cm apart is about one order of magnitude smaller than in the Wood's tube. The field ranges from 0.9 V/cm at 0.015 Torr to 4.7 V/cm at 1.5 Torr, the usable pressure range. The small radial field gradient of $\leqslant 0.3$ V/cm for a 1-cm radius from the tube axis makes it possible to expand the laser beam to 0.7 cm diam with telescopes enclosing the two polarizers (Fig. 1) reducing the dynamic Stark shift to <0.1 MHz. The He-H_2 discharge shows almost no interdependence between pressure and current for currents above 50 mA, at which current the H_2 is completely dissociated in the middle of the tube. Thus the shift and broadening due to the buffer gas density and induced by the microscopic and macroscopic electric fields in the discharge can be measured separately.[6]

An open two-wire rf transmission line is suspended in the middle of the positive column of the discharge and serves to induce the rf or microwave transitions. The small structure (0.1-cm-diam steel wires, 1 cm apart and covered with 0.2-cm-diam quartz tubes) disturbs the electric field in the positive column very little and thus the rf or microwaves can penetrate the quasi plasma between them.

Double-quantum transitions 2^2S-3^2S (-3^2D) can be observed with lockin detection by means of amplitude or frequency modulating the rf. Making use of the low-background saturated polarization method,[2] double-quantum transitions (Fig. 2) are obtained with a signal-to-noise ratio comparable to the single-photon polarization signals. Amplitude modulation of the rf (271 MHz) already results in a completely resolved dispersion-shaped double-quantum resonance signal ($2S_{1/2}, F=1 \rightarrow 3P_{1/2}, F=1 \rightarrow 3S_{1/2}, F=0$) in hydrogen of less than 20 MHz width since the rf transition $3P_{1/2}, F=0 \rightarrow 3S_{1/2}, F=0$ is forbidden. Therefore no crossover signal occurs and the $3P_{1/2}$ hfs splitting of 17.6 MHz is resolved. Taking the derivative by frequency modulating the rf, the linewidth is reduced by an additional factor of about 2.[7] For comparison, the width of the single-photon transition $2S_{1/2}$-$3P_{1/2}$, for the same conditions as in Fig. 2(a), is 72 MHz. As a test, a preliminary value for the $3S_{1/2}$-$3P_{1/2}$ Lamb shift is determined to be $-316(2)$ MHz, which is in agreement with microwave measurements.[8]

For the determination of the $3P_{3/2}$-$3D_{3/2}$ Lamb shift, the frequency difference of single- and double-quantum transitions (Table I) is also measured in reference to frequency markers of a 1-m confocal interferometer cavity which is evacuated and highly temperature stabilized. The observed splitting of the $P_{3/2}$ and $D_{3/2}$ levels is almost one order of magnitude smaller than the full width at half-maximum (FWHM) of the $P_{3/2}$ state for the experimental conditions [Fig. 2(b)].

TABLE I. Lamb shift ($3P_{3/2}$-$3D_{3/2}$) in hydrogen.

Measured frequency difference	
D_2 ($2S_{1/2}$-$3P_{3/2}$) − ($2S_{1/2}$-$3D_{3/2}$)	− 11.0(0.7) MHz
Systematic corrections[a]	
Electric field [2.23(3) V/cm]	+3.9(0.3) MHz
Discharge current (300 mA)	+1.2(0.2) MHz
Pressure [He-H_2(15%); 0.06 Torr]	− 0.2(0.1) MHz
rf power (0.5 W)	+0.3(0.2) MHz
Unresolved, partly decoupled hfs	+0.3(0.3) MHz
Lamb shift H $3P_{3/2}$-$3D_{3/2}$	
Expt.	− 5.5(0.9) MHz (this work)
	− 5(10) MHz (Ref. 12)
	− 5(4) MHz (Ref. 13[b])
Theor.	− 5.335(1) MHz (Ref. 11)

[a] For the corrections the shifts are given with changed sign.

[b] In this paper another value of − 5.88(65) MHz is given which is obtained from the combination of the measured values for $3S_{1/2}$-$3D_{5/2}$ (Ref. 13) and $3S_{1/2}$-$3P_{1/2}$ (Ref. 8) and theoretical values for the two fine-structure splittings $3P_{1/2}$-$3P_{3/2}$ and $3D_{3/2}$-$3D_{5/2}$ (Ref. 11). This procedure does not result in an experimental or true determination of the $3P_{3/2}$-$3D_{3/2}$ Lamb shift, since this shift is already included in the theoretical values for the fine-structure splittings (Ref. 11).

Therefore, two resonance conditions are possible for the double-quantum transition: the sum and the difference of the laser and the radio frequencies. Since these two resonances cannot be resolved for radio frequencies ν_{rf} smaller than the $P_{3/2}$ FWHM, the superposition of both will result to a good approximation in a single signal centered at the middle of the $D_{3/2}$ state independent of ν_{rf}. Furthermore the width of the signal will increase by 2 times ν_{rf} because the two superimposed transitions will move apart by this amount. Both of these features are observed for the double-quantum transition $2S_{1/2}$-$3D_{3/2}$ as is shown in Fig. 3.

Several systematic corrections (Table I) have been carefully determined by taking more than three hundred saturation signals. The largest correction is the Stark shift due to the macroscopic dc electric field in the discharge which can be easily measured to the given accuracy.[9] To make allowance for the uncertainty due to a small asymmetry of the single-photon D_2 signal, originating from a signal contribution of a $P_{3/2}$-state admixture to the $D_{3/2}$ level, the statistical error of $\Delta\nu$ ($3P_{3/2}$-$3D_{3/2}$) in Fig. 3(a) of ± 0.45 MHz is increased to ± 0.7 MHz. The effect of the $D_{3/2}$-state admixture to the $P_{3/2}$ level is completely negligible. The gas-discharge shift due to the microscopic electric fields of the charged particles and the pressure shift are the differences in the shifts for the single-photon and the double-quantum transitions.

For the pressure range of 0.06–0.2 Torr used, the hfs of the $3P_{3/2}$ and $3D_{3/2}$ states are partly de-

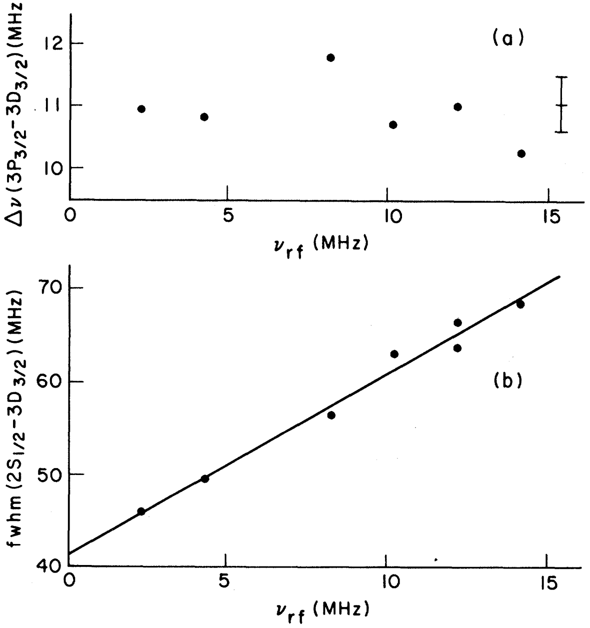

FIG. 3. (a) Frequency difference $\Delta\nu$ of the H_α D_2 $2S_{1/2}$-$3P_{3/2}$ line and the $2S_{1/2}$-$3D_{3/2}$ double-quantum resonance and (b) the FWHM of the latter as a function of the radio frequency ν_{rf}.

coupled by collisions with the buffer-gas atoms. The degree and the effect of the hfs decoupling is difficult to establish for the two $J=\frac{3}{2}$ states involved.[10] Therefore the maximum frequency difference of 0.6 MHz in the two limits of coupled or uncoupled hfs is included in the systematic corrections. The final value of $-5.5(0.9)$ MHz is in good agreement with the theory[11] and is more than a factor of 4 more accurate than previous measurements.[12,13]

In addition to this direct determination of the H $3P_{3/2}$-$3D_{3/2}$ Lamb shift the described DQS method has several further applications. For the measurement of fine-structure splittings of $n \geq 3$ hydrogen states it can in principle compete in accuracy with microwave measurements, particularly if one can make use of the population inversion discussed below. An improved value for the electron-proton mass ratio can be obtained from a determination of the H-D isotope shift at an uncertainty level of less than 0.2 MHz. The nuclear size effects are smaller by a factor of 8 in the case of the 2^2S-3^2S compared to the 1^2S-2^2S transition. A new value of the Rydberg constant[14] can be determined from both the H_α and D_α lines because the deuterium 2^2S and 3^2S hfs can be resolved by double-quantum saturation spectroscopy. Pressure and plasma shift and broadening[6] of the hydrogen 3^2S and 3^2D levels can be more easily and accurately investigated than with normal saturation spectroscopy. A complete set of these data for all $n=2$ and $n=3$ levels in hydrogen is of particular interest for the theoretical interpretation of the pressure shift in He and other buffer gases.[6] Laser-rf double-quantum spectroscopy of hydrogenic ions or high Rydberg states of other neutral or charged atoms seems to be feasible as well.

For further improvement of the precision inherent in this method it may be desirable to replace the discharge by a beam of metastable hydrogen atoms. With the present technique the accuracy can be improved considerably by running the He-H_2 discharge at pressures $p<0.01$ Torr for which the dc electric field drops well below 1V/cm, and both the pressure- and current-shift corrections are much smaller than at higher pressures. With a more highly emitting dispenser cathode than the one used, discharges can be maintained at even lower pressures. Preliminary test measurements for a He-H_2 (1%) gas mixture indicate that a population inversion of, e.g., the $3\,^2S$ or $3\,^2D$ levels over the $2\,^2P_{3/2}$ state may be achievable by means of double-quantum transitions at $p<0.01$ Torr. With sufficiently high gain, an rf-induced H_α laser may be possible with potential use in precision experiments.

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[a] On sabbatical leave from Physikalisches Institut der Universität Heidelberg, Philosophenweg 12, D-6900 Heidelberg, West Germany.

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[7] To achieve a reasonable signal strength the frequency modulation amplitude of the rf has to be of the order of the half-width of the Lamb dip in the intermediate $3P_{1/2}$ state. A differentiated 2^2S-3^2S signal of the same reduced width and similar signal-to-noise ratio is obtained by frequency modulating the laser (amplitude ± 1 to ± 5 MHz) in addition to the rf amplitude modulation and by using two lockin amplifiers in series.

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[9] The dc Stark shift is calculated for the $|m_J|=\frac{3}{2}$ levels in both the $3P_{3/2}$ and $3D_{3/2}$ states. This is justified because the circularly polarized saturation beam of > 7 mW power results in a very high $3P_{3/2}$-state polarization. Thus the $|m_F|=2$ levels are almost exclusively populated which have pure $|m_J|=\frac{3}{2}$ wave functions. Measurements carried out at higher He buffer-gas pressures (0.2 Torr) and consequently higher dc electric fields (3.1 V/cm) show the correct dc-Stark-shift dependence.

[10] A more detailed discussion of the collisional decoupling and narrowing effect is given in Ref. 6, in particular for the case of the $3P_{1/2}$ level. This effect is analogous to that observed for nuclear magnetic resonance

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Microwave Ionization and Excitation of Rydberg Atoms

J. G. Leopold and I. C. Percival
Department of Applied Mathematics, Queen Mary College, University of London, London E1 4NS, United Kingdom

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A classical theory gives excellent agreement with the Bayfield-Koch experiment on microwave ionization of Rydberg hydrogen atoms. The time dependence of excitation and ionization is presented, and classical trajectories are divided into four significant categories. The results suggest that nonresonant laser ionization of atoms in states of low quantum number can also take place as a result of extremely high-order processes with large numbers of intermediate states of excitation.

In the recent experiments of Bayfield and Koch[1] and of Bayfield, Gardner, and Koch[2] beams of highly excited hydrogen atoms were passed through a microwave cavity. The probability of ionization was measured[1] and excitation to states higher than the initial states detected.[2] The experiments were suggested by them to be a useful scaled model of laser ionization of atoms in low states.

Their experimental results can be summarized as follows: (EX1) For given field frequency (i.e., microwave) the ionization probability rises from zero to unity with increasing field strength. Considerable ionization is observed even when the peak electric field strength is small by comparison with the static electric field strength needed to ionize the atom. (EX2) The ionization probability depends on the field frequency ω_F. (EX3) Multiphoton excitations take place.

It is clear that very large numbers of quantum states are involved. The usual theories of laser ionization[3] have not been applied. The Keldysh dynamic barrier-penetration theory[4,5] is clearly inadequate because barrier penetration decreases approximately as $\exp(-n)$ and is utterly negligible for $n \approx 66$. However the parameter γ introduced by Keldysh has a classical interpretation which is important in this Letter.

In our theory both atom and microwave field are treated classically and the magnetic effects of the field neglected. While the atom is in the interior of the microwave cavity its electron moves in a classical orbit satisfying Hamilton's equations with the Hamiltonian function

$$H(\vec{r},\vec{p}) = \tfrac{1}{2}p^2 - r^{-1} + zF_{\max}\cos\omega t, \qquad (1)$$

where $\vec{r}$ is the position and $\vec{p}$ the momentum of the electron and units have been chosen for which the charge and mass of the electron are unity. Entry to and exit from the cavity are represented by adiabatic increase and decrease of the envelope of the oscillating field.

The initial conditions are chosen by a Monte Carlo method from a classical microcanonical distribution corresponding to equal population of the degenerate (l, m) states of a given n. The equations of motion are solved by stepwise numerical integration. Details of the method and checking procedures are given by Leopold and Percival.[6] The theory and method were both adapted from well-tried procedures for collision processes.[7]

The method was subject to the following errors: (E1) The precise conditions of the laboratory experiment, such as the initial distribution over (l, m) states produced by charge transfer, and the form of the rise and fall of the microwave field, were not known. (E2) The quantized atom and field are represented by a classical model. (E3) There are errors in computation, mainly inadequate statistics.

Experimental results without errors E1 were unavoidable to us, the errors E3 are probably slightly smaller, and the errors E2 are certainly completely negligible by comparison. Thus the theoretical model adequately represents the