$E(L_3)$ from Nb to Nb^{3+} and Nb^{5+} respectively.

The M, N, and O shells do not appear to be responsible for the 3.8% effect. We computed relativistic Hartree-Fock-Slater potentials for the configurations Nb, Nb^{1+}, Nb^{3+}, Nb^{5+}, and used these to generate α_{MNO}. The results are only approximate since eigenvalues were used in place of the experimental binding energies, but they do indicate that changes in α_{MNO} contribute less than 0.5% to $\Delta\lambda$.

In addition the half-life of the 122-keV radiation of ^{90m}Nb on the spots was measured yielding $T_{1/2} = 18.6 \pm 0.5$ sec. This value agrees well with the earlier result[5,6] $T_{1/2} = 18.8$ sec for ^{90m}Nb in several chemical environments. Thus even "free" Nb atoms show within the limits of error the same $T_{1/2}$ as atoms bound in metals or molecules indicating that internal conversion takes place in the L_3 and higher shells.

In conclusion this work appears to eliminate the intriguing possibility that ^{90m}Nb is a unique case where conversion in a specific inner subshell could be switched on and off by changes in chemical bonding. Only a steep drop in α_{L_3} within 10 eV of threshold would permit this, and we find no evidence for such a drop. The inconsistencies among direct and indirect measurements[1-6] of lifetime changes remain unexplained and further work in that area appears necessary. It should at least be possible to repeat the indirect measurement by Cooper, Hollander, and Rasmussen[2] of transition energy with about ± 12 eV precision. Finally the present theoretical calculation of conversion coefficients appears to be much more successful in the energy region close to threshold than its predecessors.[14]

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[1] G. T. Emery, Annu. Rev. Nucl. Sci. 22, 165 (1972).

[2] J. A. Cooper, J. M. Hollander, and J. O. Rasmussen, Phys. Rev. Lett. 15, 680 (1965), and Nucl. Phys. A109, 603 (1968).

[3] A. Olin, Phys. Rev. C 1, 1114 (1970).

[4] W. Weirauch, W. D. Schmidt-Ott, F. Smend, and A. Flammersfeld, Z. Phys. 209, 289 (1968).

[5] J. S. Geiger, R. L. Graham, and M. W. Johns, Can. J. Phys. 47, 949 (1969).

[6] F. Smend, I. Borchert, and H. Langhoff, Z. Phys. 248, 326 (1971).

[7] R. F. O'Connell and C. O. Carroll, Phys. Rev. 138, B1042 (1965).

[8] W. Bambynek, B. Crasemann, R. W. Fink, H. U. Freund, H. Mark, C. D. Swift, R. E. Price, and P. V. Rao, Rev. Mod. Phys. 44, 716 (1972).

[9] J. L. Campbell and L. A. McNelles, Nucl. Instrum. Methods 125, 205 (1975).

[10] J. S. Hansen, J. C. McGeorge, D. Nix, W. D. Schmidt-Ott, I. Unus, and R. W. Fink, Nucl. Instrum. Methods 106, 365 (1973).

[11] H. C. Pauli and U. Raff, "A computer program for internal conversion coefficients and particle parameters" (to be published).

[12] W. D. Schmidt-Ott, to be published.

[13] J. B. Ball, M. W. Johns, and K. Way, Nucl. Data Sect. A 8, 407 (1970).

[14] J. L. Campbell and B. Martin, Z. Phys. A274, 9 (1975).

Hydrogen 1S-2S Isotope Shift and 1S Lamb Shift Measured by Laser Spectroscopy*

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We measured the isotope shift of the $1S$-$2S$ transition in atomic hydrogen and deuterium to be 670.933 ± 0.056 GHz, using Doppler-free two-photon spectroscopy with a frequency-doubled, pulsed, dye laser. The Balmer-β line is simultaneously observed in saturated absorption with the fundamental dye-laser output. A comparison of the intervals $1S$-$2S$ and $2P_{3/2}$-$4D_{5/2}$ determines the Lamb shift of the $1S$ ground state to be 8.20 ± 0.10 GHz (H) and 8.25 ± 0.11 GHz (D), in agreement with the theoretical values.

We report on the first accurate measurement of the Lyman-α isotope shift for atomic hydrogen and deuterium, using Doppler-free two-photon spectroscopy of the $1S$-$2S$ transition with a frequency-doubled, pulsed, dye laser near 2430 Å.[1] The fundamental dye-laser output near 4860 Å allowed the simultaneous observation of the Balmer-β line by high-resolution saturation spectroscopy. From a comparison of the energy intervals 1S-2S and 2$P_{3/2}$-4$D_{5/2}$ we could determine the Lamb shift of the 1S ground state of hydrogen and deuterium with an accuracy better than 2%.

Previous attempts to measure these quantities[2,3] had to rely on high-resolution vacuum-ultraviolet spectroscopy of the Lyman-α line near 1215 Å. They were hampered by the large Doppler width (30 GHz for H at room temperature), by strong self-reversal observed in emission spectroscopy, and by spurious background lines in the continuum light sources used for absorption spectroscopy.

In the only reported experiment of its kind, Herzberg[3] determined the 1S Lamb shift of deuterium with about ± 15% accuracy by comparing the absolute wavelength of the Lyman-α line with its calculated Dirac value. Radio-frequency spectroscopy, which has been very successful in measurements of Lamb shifts of excited hydrogen states,[4] cannot be used for the ground-state Lamb shift because there is no nearby P level.

An entirely new approach has become possible, since it was demonstrated[1] that the metastable 2S state can be excited with high selectivity from the 1S ground state with two counter propagating laser photons, whose linear Doppler shifts cancel. This technique circumvents the technical difficulties of vacuum-ultraviolet spectroscopy; in addition it enables us to use the Balmer-β line as a closely spaced reference line for the measurement of the 1S Lamb shift. If Bohr's formula were correct, the $n = 1-2$ interval would be exactly 4 times larger than the $n = 2-4$ interval, and the two observed transitions would occur at exactly the same dye-laser frequency. The actual displacement is due to relativistic and quantum electrodynamic corrections plus some small nuclear-structure effects.[5] This scheme drastically alleviates the need for an absolute wavelength calibration and for a precisely known Rydberg constant in the computation of the Dirac line positions.

Figure 1 shows a scheme of the experimental setup, i.e., the two-photon spectrometer (top), the saturation spectrometer (middle), and the tunable dye laser with frequency marker interferometer (bottom).

The two-photon spectrometer is essentially the same as described in Ref. 1. A lithium formate crystal doubles the frequency of the dye laser to give ultraviolet pulses of about 300-W peak power. The uv beam is focused to about 0.2-mm waist diameter inside the observation chamber and is reflected back into the chamber to provide a standing wave field. The atoms are generated in a gas discharge in a mixture of H_2 and D_2 at 0.2 Torr, and carried by gas flow and diffusion into the observation chamber. The two-photon excitation is monitored by observing the collision-induced 2P-1S fluorescence at 1215 Å with a solar-blind photomultiplier (EMR 541J) through a MgF_2 window and an interference filter with 15% transmission. The collection solid angle is about 2%.

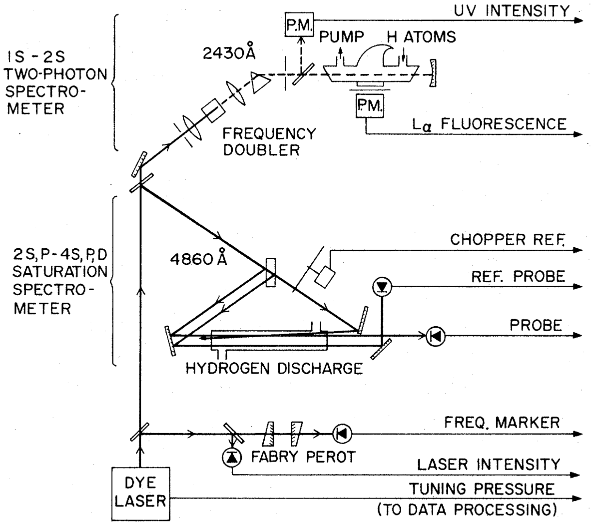

FIG. 1. Experimental setup.

The saturation spectrometer for the Balmer-β line, using a small fraction of the visible laser output, is very similar to the setup used in the study of the red Balmer-α line.[6] Two parallel weak probe beams (1.2 mm diam, 5 mW peak power) and a counterpropagating saturating beam, overlapping one of the probes (500 mW peak power, crossing angle 6 mrad), are sent through the 36-cm-long center section of the positive column of a Wood-type gas discharge ($H_2 + D_2$, 0.2 Torr, 12–15 mA). A light chopper blocks every other saturating pulse, and the two probes detect the velocity-selective hole burning in a sensitive differential detection scheme.

The pressure-tuned dye-laser system[7] operates at 17 pps and provides 10-nsec long pulses of 15-kW peak power and 120-MHz linewidth at 4860 Å. The pressure of the scan gas (N_2 or propane) is monitored with a Baratron gauge (MKS Instruments). Part of the laser output is sent through a plane Fabry-Perot interferometer to provide frequency calibration lines. The interferometer with an Invar spacer of 6.3810(1) cm length is contained in a thermally insulated air-filled housing. Corrected for the refractive index of air[8] and in the absence of thermal drifts, the separation of adjacent marker lines is 2348.47 ± 0.10 MHz.

The eight listed parameters are stored for each laser pulse in digital form on a magnetic disk memory for later computer processing.

To find the $1S$-$2S$ isotope shift, the two-photon spectrum is compared with the marker spectrum. The Lyman-α fluorescence signal is divided, pulse per pulse, by the square of the ultraviolet laser intensity, and the spectrum is obtained by sorting the normalized signal according to scan gas pressure into an array of average values with frequency increments of about 20 MHz. The marker spectrum is generated by the same sorting procedure after numerical normalization with respect to the visible laser pulse height. [Propane is used as a scan gas to allow continuous tuning across the isotope shift. The speed of the scan (always towards longer wavelength) is about 48 MHz/sec near the two-photon resonances, and about 10 times faster in between, to reduce the total scan time from D to H to about 10 min.]

Typical two-photon spectra and marker spectra, smoothed by convolution with a Gaussian profile of three channels width, are shown in Fig. 2. The hydrogen spectrum shows the expected hyperfine doublet; the corresponding splitting for deuterium is about 4 times smaller and unresolved.

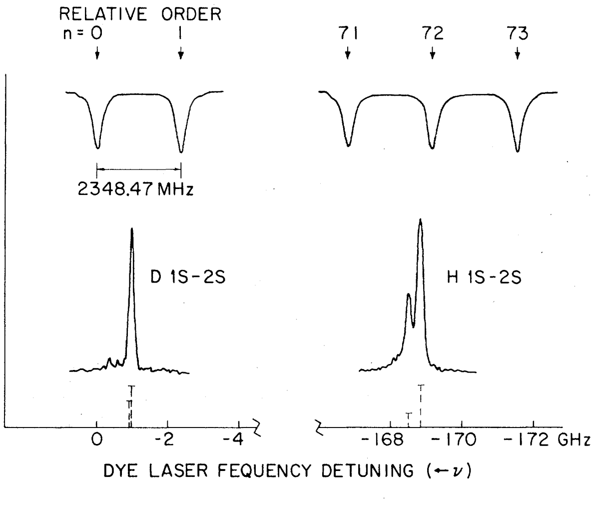

FIG. 2. Doppler-free two-photon spectra of the $1S$-$2S$ transition in H and D with transmission maxima of the calibration interferometer.

The isotope shift is determined by measuring the separation of the numerically calculated centers of gravity of the two-photon resonances in terms of fractional orders of the marker spectrum. No attempt is made to treat the two hydrogen-line components separately, since the hyperfine splitting does not shift the center of the doublet.

Eight individual spectra were numerically evaluated. The expected systematic shifts of the two-photon resonances due to ac Stark effect (1 MHz)[1] and second-order Doppler effect (50 kHz) are quite negligible. Thermal drifts of the calibration interferometer are a more serious problem. A linear long-term drift up to 2 ± 1 MHz/min was found from a comparison of spectra recorded at different times, and a corresponding correction was applied to the marker frequency scale. The resulting systematic uncertainty of 6 parts in 10^5 is of the same magnitude as the statistical standard deviation, and is included in the rms error of the final results. We obtain a $1S$-$2S$ isotope shift of 670.933 ± 0.056 GHz, which represents an improvement of several orders of magnitude over previous measurements of the Lyman-α isotope shift[2] and is in fair agreement with the theoretical value[9] of 670.994 ± 0.0008 GHz.

The determination of the $1S$ Lamb shift requires the simultaneous recording of the saturation spectrum of the Balmer-β line. The saturation signal, given by the intensity difference of the two probe beams, is corrected for nonideal probe balancing,[6] and again sorted into an array of average values. A typical saturation spectrum for hydrogen, together with the simultaneously recorded $1S$-$2S$ two-photon spectrum and marker spectrum, is shown in Fig. 3. N_2 was used as scan gas, and the typical tuning rate was 44 MHz/sec. The relatively large linewidths of about 500 MHz in the saturation spectrum are partly caused by power broadening due to the strong saturating beam, which is required to obtain an acceptable signal-to-noise ratio at the utilized low pulse rates.

To measure the frequency separation between the $1S$-$2S$ resonance and the strong $2P_{3/2}$-$4D_{5/2}$ component at the right-hand side of the saturation spectrum we use the numerically calculated centers of gravity of the two-photon doublet, and of that part of the Balmer-β fine-structure line which reaches above half maximum. The cutoff level reduces line shifts due to weak unresolved neighboring line components. For hydrogen, we obtain a line separation of 3.408 ± 0.026 GHz

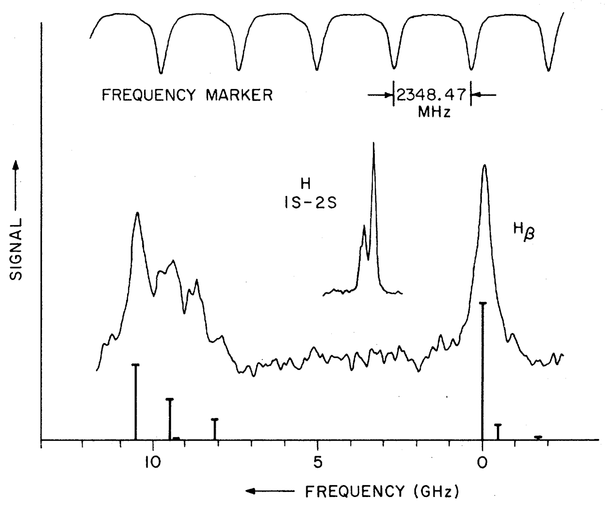

FIG. 3. Saturation spectrum of the hydrogen Balmer-β line with theoretical fine-structure spectrum, and simultaneously recorded 1S-2S two-photon spectrum. The top curve gives the resonances of the calibration interferometer.

from 24 evaluated spectra, and for deuterium a separation of 3.398 ± 0.027 GHz from 9 spectra. These values have been corrected for systematic shifts in the saturation spectrum, and the quoted rms errors contain the estimated systematic uncertainties. The statistical standard deviations are 0.009 and 0.005 GHz, for comparison. In particular, a correction of − 5 ± 3 MHz has been applied to correct for an expected dc Stark shift in the field of the positive discharge column (10 V/cm). Corrections of + 9 ± 4 MHz for H and + 13 ± 6 MHz for D account for the estimated ac Stark shift[6] due to the interaction of the strong saturating beam with the neighboring $2P_{3/2}$-$4D_{3/2}$ transition. An upper limit for possible pressure shifts of ± 14 MHz was established by measurements between 0.15 and 0.5 Torr. An additional correction of + 19 ± 19 MHz for H and + 22 ± 22 MHz for D takes into account the expected line shift due to the blending of the $2P_{3/2}$-$4D_{5/2}$ component with its weak $2P_{3/2}$-$4D_{3/2}$ neighbor, situated 460 MHz towards the red, and with the expected intermediate crossover line.[6] The respective relative heights of these unresolved components have been estimated to be 3.5 and 7% from a comparison with the saturation spectrum of the Balmer-α line[6] which has the same relative oscillator strengths, but a larger fine-structure splitting, so that the corresponding line components can be resolved. Finally, we have made a correction of + 2 ± 2 MHz for hydrogen to account for unresolved hyperfine structure and associated crossover lines.[6]

The corresponding theoretical frequency separations according to recent calculations by Erickson[9] are 3.420 967(87) GHz (H) and 3.417 92(12) GHz (D), assuming a theoretical 1S Lamb shift of 8.149 43(8) GHz (H) and 8.172 23(12) GHz. From a comparison between the experimental and theoretical line separations, we determine a 1S Lamb shift of 8.20 ± 0.10 GHz for H and 8.25 ± 0.11 GHz for D. Both values agree within their error limits with the theoretical values.

Considerable improvement in accuracy should be possible, if the resolution of the 1S-2S two-photon spectrum is improved by reducing the laser linewidth (a laser power of 1 mW should be sufficient in a cw experiment), and if the resolution of the Balmer-β line is improved, e.g., by Doppler-free two-photon spectroscopy of the 2S-4S, *D* transitions. The latter could for instance be accomplished with a GaAs diode laser, whose second harmonic is locked to the visible dye-laser frequency. Since neither linewidth is limited by a short living *P* state, the ultimate accuracy of such a measurement could well exceed that of recent 2S Lamb shift measurements,[4] or even that of present calculations, which are limited by our knowledge of the fine-structure constant and of nuclear-structure effects. In addition, there is presently a discrepancy between different computational approaches[10] which makes precise Lamb shift measurements highly desirable.

The large isotope shift is primarily caused by the nuclear mass difference[5] and the accuracy of present calculations is limited by the uncertainty of the ratio of electron mass m_e to proton mass m_p (1 ppm). The uncertainty of the fine-structure constant and of the nuclear-size effect contributes only at the 0.1 ppm level. Since the ratio of proton mass to deuteron mass is known to 0.01 ppm, future, more precise, measurements of the 1S-2S isotope shift promise to provide a precise value of the important ratio m_e/m_p. Together with other precision experiments, the envisioned measurements should permit stringent new consistency tests of quantum electrodynamics.

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[1] T. W. Hänsch, S. A. Lee, R. Wallenstein, and C. Wieman, Phys. Rev. Lett. 34, 307 (1975).

[2] S. S. Ballard and H. E. White, Phys. Rev. 43, 941 (1933).

[3] G. Herzberg, Proc. Roy. Soc. London, Ser. A 234, 516 (1956).

[4] S. R. Lundeen and F. M. Pipkin, Phys. Rev. Lett. 34, 1368 (1975).

[5] J. D. Garcia and J. E. Mack, J. Opt. Soc. Am. 55, 354 (1965).

[6] T. W. Hänsch, M. H. Nayfeh, S. A. Lee, S. M. Curry, and I. S. Shahin, Phys. Rev. Lett. 32, 1336 (1974).

[7] R. Wallenstein and T. W. Hänsch, Opt. Commun. 14, 353 (1975).

[8] H. Barrell and J. E. Sears, Trans. Roy. Soc. (London) A238, 1 (1933).

[9] G. Erickson, private communication.

[10] P. J. Mohr, Phys. Rev. Lett. 34, 1050 (1975).

Dynamical Resonances in Collinear, Coplanar, and Three-Dimensional Quantum Mechanical Reactive Scattering*

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We present results of one-, two-, and three-dimensional calculations for the $H + H_2$ exchange reaction which provide the first evidence for dynamical internal excitation (Feshbach) resonances in chemical reactions using noncollinear calculations. The change of the resonance energy and width with collision dimensionality and with total angular momentum is analyzed and indicates the existence of observable effects on certain reactive cross sections.

Internal excitation resonances have been observed in a large number of diverse collision phenomena including π-p scattering,[1] electron-atom and electron-molecule scattering,[2] and (theoretically) rotationally inelastic atom-molecule scattering,[3] but they have yet to be detected in atom-diatom reactive scattering experiments. Their existence has previously been established theoretically only in collinear models of these simple chemical reactions.[4-8] The results of those collinear calculations indicate that these resonances are responsible for oscillations in the reaction probabilities near the resonance energies through their interference[8] with the direct mechanisms. However, because of partial-wave averaging, it was not known whether such resonances would exist in the three-dimensional (3-D) world. We present here the results of accurate quantum mechanical calculations for 1-D, 2-D, and 3-D collisions for the historically important $H + H_2$ exchange reaction which provide the first evidence for dynamical resonances in chemical reactions for noncollinear systems. An understanding of the relation between the characteristics of such resonances and the nature of the potential surfaces which give rise to them may prove a sensitive probe in the experimental characterization of these surfaces and in the development and testing of approximate reaction-dynamic theories.

The methods used for solving the Schrödinger equation for the collinear, coplanar, and three-dimensional $H + H_2$ collisions are the same as those we developed and used previously.[8-11] In order to obtain accurate results in the 2-D and 3-D calculations at the relatively high energies at which the resonances were found, quite large vibration-rotation basis sets were required, involving five or six vibrations and rotational quantum numbers $j = 0-6$ to $j = 0-9$ for each vibration for a total of sixty coplanar channels (for all values of total angular momentum quantum number J), and 40 to 90 ($J = 0, 1$) 3-D channels. For most of these noncollinear calculations, tests of conservation of flux, microscopic reversibility, and invariance with respect to number and choice of expansion functions indicated convergence of 5 to 10% although a few poorer results (20%) were included. The collinear results, for which ten vibrational basis functions were used, are accurate to 0.5% or better. The Porter-Karplus[12] potential energy surface was used for all calcula-