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Singlet-triplet mixing in the 13*d* Rydberg state of ^{3}He observed with stepwise laser excitation

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The hyperfine structure of the singlet and triplet 13*d* Rydberg states in ^{3}He have been studied by stepwise excitation with a single-mode uv laser (294.5 nm) and single-mode color-center laser (2.590 μm). The experimental results for the 13*d* state are in good agreement with semiempirical calculations. No difference in the electrostatic energy interval was found between the ^{3}He and ^{4}He atoms, in contrast to earlier measurements for $n=5-8$ states.

Perturbations of Rydberg states due to electron-electron interactions with close lying states have been investigated in great detail in alkaline-earth atoms.[1] In ^{3}He Rydberg states, perturbations due to singlet-triplet induced fine and hyperfine (hf) mixing play an important role. Although the ^{3}He atom is the simplest two-electron system for the study of electron-electron interactions, no previous measurements in states with principal quantum numbers $n > 8$ exist. The investigations in the alkaline-earth atoms were performed by laser spectroscopic techniques employing laser excitation from the ground state. In the ^{3}He atom, laser excitation must start in the metastable 2*s* levels. Until now, this has prevented successful investigation by high-resolution laser spectroscopy of higher excited states.

The recent extension of cw dye lasers into the ultraviolet range by efficient frequency doubling has made it possible to study high-lying Rydberg states in ^{3}He by stepwise laser excitation spectroscopy. Using a single-mode cw dye ring laser to pump an external frequency doubler inside a passive enhancement cavity, we have populated the $1s5p\ ^3P$ state of ^{3}He by excitation from the metastable $1s2s\ ^3S$ state at 294.5 nm. In a second step, an infrared single-mode color-center laser is used to excite *s* and *d* Rydberg states with principal quantum numbers $n \geqslant 12$. With the laser beams oriented parallel or antiparallel, the experiment yields spectra free of Doppler broadening.[2] In this Communication, we report on stepwise excitation spectroscopy of the singlet and triplet Rydberg *d* states of ^{3}He. A detailed analysis is given for 13^1D and 13^3D levels and the experimental results are compared with semiempirical calculations involving the diagonalization of the fine plus hf Hamiltonian for the singlet-triplet *d* subspace.

There exist only a few accurate measurements of the hf structure of the excited levels of ^{3}He. The splittings in the $n\ ^3S$ and $n\ ^3D$ states ($n=3-6$) have recently been measured by optogalvanic spectroscopy,[3] by intermodulated fluorescence spectroscopy,[4] and by Doppler-free two-photon spectroscopy[5] with the help of visible cw dye lasers. The hf constants of the $n\ ^3P$ states ($n=2-4$) were measured by the optical microwave method[6] and by beam-foil spectroscopy.[7] The hf constants of the $5\ ^3P$ states were investigated by intermodulated fluorescence spectroscopy with the same single-mode uv laser used in this experiment.[8] A few selected hf splittings in the $n\ ^3P$ ($n=3-8$), $n\ ^1D$, and $n\ ^3D$ ($n=3-7$) states were measured by level crossing spectroscopy.[9] Anticrossing spectroscopy provided results on the singlet-triplet splittings of the $n\ ^1D-n\ ^3D$ ($n=3-8$) intervals.[10, 11]

The tunable ultraviolet radiation for the present experiment is produced by frequency doubling the output of an actively stabilized rhodamine 6G dye ring laser (Coherent Inc. 699-21) in a 23-mm-long 90° phase-matched ammonium dihydrogen arsenate crystal inside a passive ring resonator. With 1.5 W of output power, over 50 mW of ultraviolet power could be extracted.[8] The color-center laser, a modified Burleigh FCL-20 laser, is described in Ref. 12. For reliable single-mode stability, an additional solid etalon of 3-mm thickness has been inserted into the cavity. Using a KCl:Li crystal, the color-center laser produces 15 mW of infrared radiation near 2.6 μm when pumped by the 1-W output beam of a broadband dye laser at 600 nm. Both lasers have a frequency bandwidth of less than 2 MHz.

The ^{3}He atoms in the metastable $2\ ^3S$ level are produced by bombardment of ground-state atoms with electrons of 50-eV energy from an electron gun.[13] The two laser beams counterpropagate through the interaction region at a distance 25 mm from the electron beam. The infrared radiation is chopped at a frequency $f_m = 1440$ Hz. The stepwise excitation signal is recorded by observing a modulation frequency f_m in the fluorescence at the uv-excitation wavelength, emitted from the intermediate 5^3P state.

Figure 1 shows a Doppler-free stepwise excitation scan of the $2^3S-5^3P-13^{1,3}D$ transition in ^{3}He with all strong hf components. The spectrum was recorded at 35-mTorr pressure with an ultraviolet power of 25 mW and an infrared power of 5 mW. For this scan, the single-mode uv laser was positioned at the center of the absorption profile of the $2\ ^3S-5\ ^3P$ transition

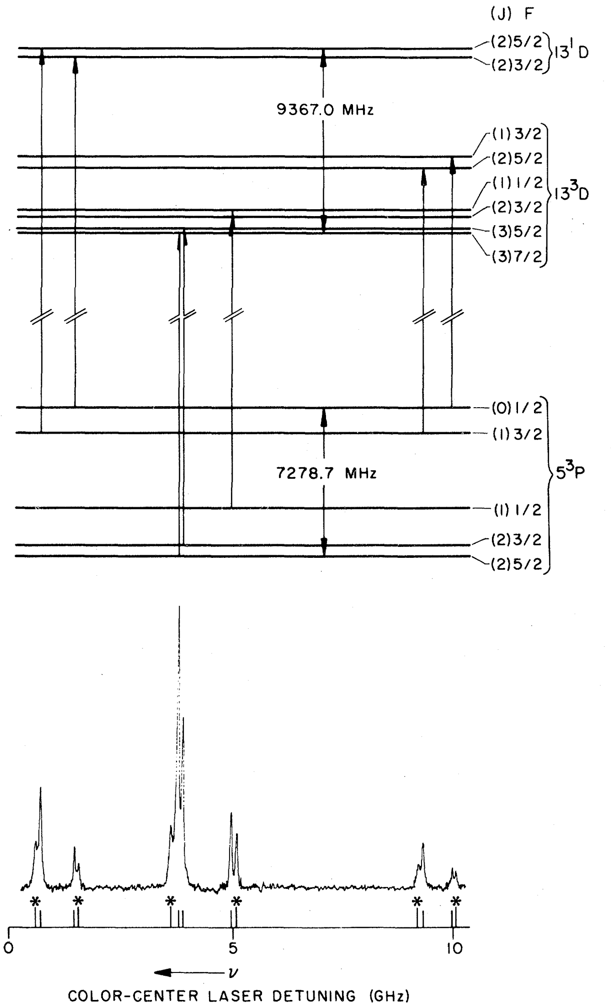

FIG. 1. Doppler-free stepwise excitation scan of the $2\,^3S-5\,^3P-13\,^{1,3}D$ transition in ^{3}He. Lines marked by a star are collisionally induced hf transition peaks. In a level diagram (not to scale) of the $5\,^3P$ and $13\,^{1,3}D$ states, above the spectrum, we have indicated the transitions corresponding to observed components.

by actively locking to a stabilized Fabry-Perot resonator. The color-center laser was scanned across the hf components of the $5\,^3P-13\,^{1,3}D$ line. The lock-in signal is Doppler-free because the single-mode uv laser excites the $5p$ hf levels in small velocity intervals only.[2] Frequency measurement was accomplished using a confocal infrared interferometer with a free spectral range of 149.82 ± 0.05 MHz. The measured hf intervals were corrected for frequency shifts due to the excitation of different velocity intervals in the hf levels of the $5\,^3P$ state. The energy values obtained are the averages of many measurements. The lines marked with a star are additional peaks caused by collisions which induce hf transitions in the $5p$ state. Since these peaks have almost the same linewidth as the hf lines, it is obvious that the velocity of the atoms remains virtually unchanged. The height and width of these peaks are pressure dependent and could be used as a sensitive probe for investigation of collisional processes.

The assignment of the spectrum cannot be done in a $LS(J)I,F$ coupling scheme. J is not a good quantum number due to singlet-triplet mixing and the strong hf interaction of the $1s$ electron with the nuclear spin. We have calculated the eigenvalues and relative intensities for the $13d$ subspace in an uncoupled representation and compared them with the observed spectrum. The energy values for the $5p$ state were obtained in a separate experiment with an accuracy of 1 MHz.[8] The Hamiltonian for the $13d$ subspace is given by

$$H = H_0 + H_{\mathrm{fs}} + H_{\mathrm{hfs}} \;. \tag{1}$$

H_0 determines the energy of the spinless electron. We assume H_0 to be diagonal in the uncoupled basis and the separation $13\,^1D-13\,^3D = E_0$, sometimes called the electrostatic energy separation, is approximated by the value obtained for the ^{4}He atom.[14] The fine-structure Hamiltonian for a two-electron atom in parametrized form is given by[15]

$$H_{\mathrm{fs}} = A\vec{L}\cdot\vec{S} + a\vec{L}\cdot\vec{K} + b\left[\frac{3(\vec{L}\cdot\vec{S})^2 + \frac{3}{2}\vec{L}\cdot\vec{S} - \vec{L}^2\cdot\vec{S}^2}{2S(2S-1)L(2L-1)}\right] , \tag{2}$$

where

$$\vec{L} = \vec{l}_1 + \vec{l}_2 \;,\quad \vec{S} = \vec{s}_1 + \vec{s}_2 \;,\quad \vec{K} = \vec{s}_1 - \vec{s}_2 \;,$$

and A, a, and b are the spin-orbit, the spin-orbit singlet-triplet, and the spin-spin coupling constants, respectively. For the hf Hamiltonian of the $13d$ state, the parametrized form is given by

$$H_{\mathrm{hfs}} = C\vec{I}\cdot\vec{S} + C\vec{I}\cdot\vec{K} \;, \tag{3}$$

where both terms describe the Fermi contact interaction. In the $13d$ state, the nuclear-spin electron-spin-orbit interaction can be neglected. Singlet-triplet mixing is given only by the antisymmetric $\vec{L}\cdot\vec{K}$ and $\vec{I}\cdot\vec{K}$ terms. The contribution for the Fermi contact term results from the spin density of the $1s$ electron at the nucleus. Therefore both terms in Eq. (3) have the same coupling constant C and are independent of the quantum number n of the excited electron. Since the $n\,^1D-n\,^3D$ separation decreases with increasing n, perturbations due to singlet-triplet mixing become more effective at higher n levels.

Calculations of the hf splittings of the ^1D levels of ^{3}He were carried out by Bessis *et al.*[16] by using the hydrogenic approximation for the states $n = 3-8$.

With the hydrogenic constants calculated for the $13d$ state and the experimentally determined value

E_0, we have obtained eigenvalues by diagonalizing the complete Hamiltonian matrix for the 13d subspace. In Table I, first row, we list the eigenvalues as calculated. The use of experimentally determined ^{4}He fine-structure constants gives insignificantly different results. For comparison, the energy values of the 13d state in ^{4}He are listed in row 3, as calculated by omitting the hf interaction from the Hamiltonian. The influence of singlet-triplet mixing in ^{3}He is clearly seen. For instance, the two singlet levels are shifted about 7 GHz to higher frequencies. The classification of the 13d level of ^{3}He into singlet and triplet states is thus artificial and only used to identify the different hf components. In ^{4}He, singlet-triplet mixing alters the value of the electrostatic fine-structure interval by about 60 kHz only. Therefore the uncorrected E_0 value can be used.

With the help of the calculated eigenvalues and the hf splittings of the 5 ^3P state[8] the assignment of the spectrum is possible (see Fig. 1). The hf intervals in the spectrum are given by the sum or difference of splittings of the 13d and 5 ^3P states. These intervals vary from a hundred MHz to several GHz. Thus, despite an experimental linewidth of about 35 MHz, it is possible to obtain results on d-state splittings of a few MHz. In the second row of Table I, we list the energies of the 13 ^1D and 13 ^3D levels, measured with respect to the (3)$\frac{7}{2}$ hf component. The calculated and measured values agree within the experimental uncertainty of at most 4 MHz.

With eigenvector matrices calculated for the 5 ^3P and 13d states, we have computed the intensities of the hf components. The intensity of the 5p-13d line is concentrated in a few components due to the strong mixing, a fact which greatly simplifies the spectrum. The components appearing in Fig. 1 are the only transitions which are predicted to have significant intensity and differ from calculated transition probabilities by at most a few percent.

The agreement found between calculation and measurement is well within the experimental error, indicating that the use of hydrogenic wave functions is sufficiently precise at an uncertainty level of a few MHz. Significantly, we have found no deviation of the electrostatic energy interval E_0 between ^{3}He and ^{4}He. Investigations on the 3 ^3D and n ^3D (n = 3–6) states by intermodulated fluorescence spectroscopy[4] and two-photon spectroscopy,[5] respectively, have also shown good agreement with calculated hf structure. For the fine- and hf-structure constants, either hydrogenic or experimentally determined values have been used. The electrostatic energy intervals ^1D-^3D of ^{3}He have been observed by anticrossing spectroscopy for n = 3–8.[10,11] For the states n = 5–8, a systematic difference between the ^{3}He and ^{4}He intervals of $E_0(^3\mathrm{He}) - E_0(^4\mathrm{He}) > 30$ MHz was found. Anticrossing spectroscopy provides results only on the electrostatic interval so that other results cannot be compared. No mechanism has been found which can explain this difference in the singlet-triplet interval of the d states between the two helium isotopes. In all cases, the best known electrostatic energy intervals of the ^{4}He d states[14] were compared with the ^{3}He intervals. Our measurement of the 13 $^{1,3}D$ state does not confirm such a difference. If there is any mechanism which produces a difference in the n = 5–8 states, it is apparently absent in the 13d state.

In conclusion, we have shown that by stepwise ex-

TABLE I. Energy values for the hyperfine components of the 13d level in ^{3}He and ^{4}He. The zero value corresponds to the 13^3D level in the absence of fine and hyperfine contributions. The ^{4}He results are obtained from Ref. 14. Numbers are given in MHz.

			^{3}He			^{4}He
	(J)	F	Theory	Experiment	J	Fitted results
13^1D	2	$\frac{5}{2}$	7199.2	7196.7 ±4.0	2	2269.0
	2	$\frac{3}{2}$	7182.6	7180.7 ±4.0		
13^3D	1	$\frac{3}{2}$	−575.4	−578.6 ±4.0	1	13.4
	2	$\frac{5}{2}$	−600.8	−602.6 ±4.0	2	−2.7
	1	$\frac{1}{2}$	−2153.0	−2155.6 ±3.0	3	−3.9
	2	$\frac{3}{2}$	−2161.0	−2163.6 ±3.0		
	3	$\frac{5}{2}$	−2169.4	−2168.2 ±3.0		
	3	$\frac{7}{2}$	−2170.3	−2170.3		

citation with a single-mode color-center laser and the frequency-doubled output of a single-mode dye laser, precision Doppler-free measurements in Rydberg levels of ^{3}He can be carried out. The experimental results for the 13 $^{1,3}D$ state are in excellent agreement with semiempirical calculations using hydrogenlike wave functions. The singlet-triplet mixing in the $13d$ states is so strong that transitions from the 5 ^3P to the 13 ^1D and 13 ^3D have comparable intensities. No difference in the electrostatic energy interval was found between the ^{3}He and ^{4}He, within an experimental uncertainty of a few MHz.

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