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Singlet-triplet anticrossings in He. II. The $n=6,7,8$ $^{1,3}D$ states

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The method of singlet-triplet level anticrossing has been extended to the $n = 6$ $^{1,3}D$ levels of He. Measurement of this anticrossing gives a highly accurate determination of the zero-field singlet-triplet separation and a less accurate determination of the antisymmetric part of the spin-orbit coupling perturbation between the $n = 6$ $^{1,3}D$ states. The zero-field separation for $n = 6$, although considerably more accurate, is in essential agreement with previous optical results, confirming the accuracy of the intercombination line measurements. The singlet-triplet intervals calculated by many-body perturbation theory are also found to be in very good agreement with the experimental results.

I. INTRODUCTION

In a recent paper[1] we reported the first observations of an anticrossing signal between a triplet and a singlet state. These observations were in the $n=7$ and 8 $^{1,3}D$ states of the He atom. Subsequent reports of singlet-triplet anticrossings in the H_2 molecule have recently been made.[2,3] To obtain the results on H_2, we had to modify our apparatus to increase its field capability from ~14 to 20 kG. It then became possible to measure the $n=6$ $^{1,3}D$ anticrossing in He.

The $n=6$ $^{1,3}D$ anticrossing measurement is important in two respects. It makes possible further comparison with the theoretical predictions of the $^{1,3}D$ intervals by Poe and Chang.[4-6] Secondly, in the earlier paper[1] we noted that the singlet-triplet D interval determined by the anticrossing technique for both $n=7$ and 8 was ~1.2 GHz smaller than the best, but less accurate, optical experimental results.[7] This consistency in the errors led us to consider the possibility that Herzberg's measurements[8] of the vacuum ultraviolet intercombination lines were slightly in error, giving rise to an error in the absolute energies of all the triplet states. The $n=6$ state measurement is important in deciding this question as it provides not only a third test, but one for which the optical data should be more reliable.

II. EXPERIMENTAL

In our previous work[1] on singlet-triplet anticrossings in He, we described two separate experimental apparatuses which were used to observe anticrossings signals. For the present experiments we have further modified the original apparatus (the one used for MOMRIE experiments). The vacuum chamber has been replaced by one of the same general design but small enough to fit in a $2\frac{5}{8}$-in. magnet gap. This smaller gap allows an increase of our maximum magnetic field from ~14 to ~20 kG.

A new water-cooled copper cell contains helium and supports a new electron source. $\frac{1}{2}$-in.-diam quartz light pipes extend horizontally into the cell from both directions along an axis perpendicular to the magnetic field. The new electron source consists of a 1-cm^2-area nickel matrix cathode with a $BaSrCO_3$ coating and a tungsten grid $\frac{1}{2}$ mm from the cathode. Electrons enter the cell through a hole the size of the cathode, travel about 3 cm along the magnetic field, and strike a collector on the far side of the cell. Approximately a tenfold increase in total electron current can be achieved with this gun, relative to previous models, at approximately the same current density. Thus the total emission signal can be much larger, with Stark effects less important. Alternately, with low currents Stark effects are negligible.

The data for $n=6$ $^{1,3}D$ He quoted in this paper were all taken at essentially the zero-pressure zero-current limit. Both the line positions and widths can suffer pressure effects. Measurements of linewidths were made in the 1-20-mTorr range. The higher-pressure runs showed significant broadening; a rough measure of ~3 G/mTorr for the pressure-broadening coefficient was obtained from these data. Likewise, a shift in the center of the line at a rate of ~0.6 G/mTorr was noted. The reported data were all taken in the 1-2-mTorr region where pressure effects (based upon the above coefficients) should be much less than the experimental error in the line-position and width measurements.

In the same way, empirical plots of line position and width versus gun current gave, respectively, broadening and shift parameters of ~3 G/mA and ~ -1 G/mA. The final results were obtained at currents $\leq$1 mA, so Stark shifts and broadening should be negligible.

III. THEORY

The exposition of the theory given in I for the $n=7$ and 8 $^{1,3}D$ He anticrossings is also applicable to $n=6$. Again the perturbation responsible for the anticrossing is the antisymmetric portion of the spin-orbit coupling operator. The explicit form of this perturbation is given in Eq. (7) of I. The $n=6$ $^{1,3}D$ zero-field separation has been obtained by optical experiments as ~0.69 cm^{-1} =21 GHz. The Zeeman tuning effect is given by the difference in the electron spin (g_S) and orbital angular momentum (g_L) factors. Taking $g_S = 2.00232$ and $g_L = 1 - m/M = 0.99986$ gives an effective g factor of $g_L - g_S = -1.00246$ or $\mu_B g_e/h = -1.4030$ MHz/G. Thus one would expect the $n=6$ $^{1,3}D$ anticrossing to occur at ~15 kG.

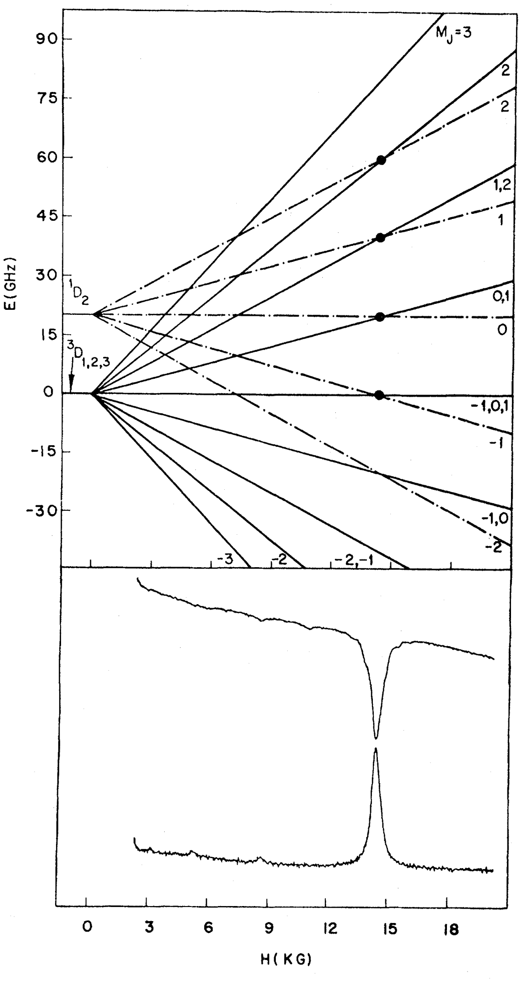

FIG. 1. Energy-level diagram (top) of the $n=6$ $^{1,3}D$ states as a function of magnetic field and actual spectra (bottom) of the $n=6$ $^{1,3}D$ anticrossing. Each of the spectral traces was obtained in approximately 10 min running time. Top trace shows the decrease in light intensity of the 6 ^1D emission line at 4144 Å, while the lower trace shows the corresponding increase in the 6 ^3D emission at 3819 Å.

As Fig. 1 shows, there are actually four distinct anticrossings between singlet states with $M_L = 2, 1, 0, -1$ and triplet states with $M_L' = M_L - 1$. In the first approximation these anticrossings are degenerate, but there are several second-order effects which lift this degeneracy. It turns out that the second-order effects are insufficient to split the observed anticrossing (Fig. 1), but they can cause small shifts in its center position and slight broadening. To determine most accurately the zero-field separation and the perturbation, these terms must be taken into account.

The diagonal spin-orbit and spin-spin interactions in the ^3D state cause its threefold zero-field separation, with $J=1$, 2, and 3 and intervals $\Delta\nu_{23}$ and $\Delta\nu_{13}$. The zero-field intervals yield the fine-structure parameters A (spin-orbit) and b (spin-spin) which are necessary to calculate the high-field shifts and broadening. The relationships are

$$\Delta\nu_{13} = \tfrac{5}{8}b - 5A, \tag{1}$$

$$\Delta\nu_{23} = -(3A + \tfrac{9}{8}b). \tag{2}$$

It may be noted that in I the sign before $\frac{9}{8}b$ was negative; this was a misprint. Fortunately, the correct equation was used in the data analysis. Using the experimental results[9-11] of $\Delta\nu_{23} = 12.2 \pm 0.3$ MHz and $\Delta\nu_{13} = 168 \pm 2$ MHz allows us to obtain $A = -26.2 \pm 0.3$ MHz and $b = 59.1 \pm 0.8$ MHz. The hydrogenic theory of Bethe and Salpeter[12] predicts $A = -27$ MHz and $b = 43$ MHz. The experimental values of A and b can be inserted into Eq. (19) of I to determine the second-order shifts due to fine structure for each M_L level of the ^3D state. These results are listed in Table I.

Besides the fine structure there are the quadratic effects of the external magnetic field. The anisotropy of the diamagnetic Zeeman interaction gives rise to a shifting of the M_L levels. We can calculate[1,12] the anisotropy coefficient χ_A using hydrogenic theory and find $\chi_A = -82.5$ mHz/G^2. Using this value we can calculate[12] the effect upon each

TABLE I. Numerical values for the difference (singlet minus triplet in MHz) in the levels M_L, $M_S=0$ of the singlet and $M_L - 1$, $M_S = 1$ of the triplet state ($n=6$) at the anticrossing field.

Singlet M_L	Quadratic Zeeman	Fine structure [a]	Motional Stark	Total
2	27.5	41.1	0.8	69.4
1	9.2	29.6	0.7	39.5
0	−9.2	−11.5	0.7	−20.0
−1	−27.5	−82.2	0.9	−108.8

[a] See footnote to Table III.

TABLE II. Relative intensities of emission from the $^{1,3}D$ anticrossing levels for a detector located at 90° with respect to the magnetic field. (Calculated from Ref. 13, pp. 63 and 91.)

Singlet M_L	Singlet I	Triplet M_L	Triplet I
2	6	1	9
1	9	0	10
0	10	−1	9
−1	9	−2	6

M_L level and the results are given in Table I.

Finally, there is the relativistic electric field derived from the motion of the He atoms in the magnetic field. (Other electric fields due to electron current, space charge, etc., have been empirically removed by extrapolating our results to zero electron current.) The effective[1] electric field for 300°K He at 15 kG is ~17 V/cm. This value and the formalism developed in I give the Stark shifts listed in Table I.

The final theoretical point involves the deconvolution of the experimental line shape, which contains four components. In order that the deconvolution be accurate one must know the relative contributions made by the four component lines. These contributions in turn depend upon the relative size of the perturbation (in Hz) and the reciprocal lifetime of the states involved. Specifically, we have stated[1] that if

$$2f_\tau |V_{SM,TM'}| \gg \hbar \bar{\tau}^{-1}, \tag{3}$$

where

$$f_\tau = (\tau_S \tau_T / \bar{\tau}^2)^{1/2}, \tag{4}$$

$|V_{SM,TM'}|$ is the spin-orbit perturbation between $^{1,3}D$ states, and

$$\bar{\tau}^{-1} = \tfrac{1}{2}(\tau_S^{-1} + \tau_T^{-1}), \tag{5}$$

with τ_S and τ_T the radiative lifetime of the singlet and triplet states, respectively, then intensities of all four anticrossings are essentially equal. This statement is true if one observes emission over all angles; however, experimentally radiation is only observed at an angle of 90° with respect to the magnetic field. The light-collection efficiency at this angle is not quite equal for all four pairs of M levels undergoing anticrossings. Using the angular dependence of polarized radiation,[13] we obtain the relative intensities listed in Table II. It is well to point out that the numbers in Table II are still subject to two assumptions. First, we assume that our detection system is equally efficient for light polarized parallel and perpendicular to the magnetic field. As the first element of our optical system is a quartz light pipe which is an efficient polarization scrambler, this assumption is probably fulfilled. Second, as mentioned previously,[1] we assume all M_L states are equally populated, which is certainly not exactly true. The difference probably affects the intensities less than the angular dependence does; since we could make neither a measurement nor a theoretical prediction of this difference, we assume all M_L levels to be equally populated.

IV. RESULTS

Measurements on the 6 ^1D and 6 ^3D anticrossing signals were made. The average of the measurements was 14899 ±15 G (zero-pressure and zero-current limit).[14] This field corresponds to a frequency of 20903 ±21 MHz, assuming the effective g factor of −1.00246. If we weight the second-order shifts given in Table I by the computed line intensities in Table II (averaged over the singlet

TABLE III. Anticrossing field positions and derived singlet-triplet intervals in the n = 6, 7, and 8 D states of He.

	Field position (G)	Singlet-triplet energy separation (MHz)	Singlet-triplet separation (MHz) with second-order correction
6*d*	14 899 ± 15	20 903 ± 21	20 906 ± 21
7*d*	9710 ± 20	13 624 ± 28	13 625 [a] ± 28
8*d*	6750 ± 25	9470 ± 35	9469 [a] ± 35

[a] These values represent a recalculation based on the data of I but correcting a mistake in the second-order effects. In Eq. (19) of I, the numerator of the expression multiplying b should be $[3M_L^2 - L(L+1)][3M_S^2 - S(S+1)]$. Making this substitution, using the weighting factors in Table II, and correcting a numerical error in the earlier work gives the above result. The changes are comparable to the experimental error and in no way affect any of the conclusions of I.

TABLE IV. Values for experimental linewidths, $|\mathcal{A}|f_T$, and values derived therefrom for the $n=6$, 7, and 8 $^{1,3}D$ states of He.

	6*d*	7*d*	8*d*
ΔH (G)	390 ± 20	254 ± 20	180 ± 20
$\Delta\nu$ (MHz)	547 ± 28	356 ± 28	253 ± 28
$\lvert\mathcal{A}\rvert f_T$	77.5 ± 4.0	50.5 ± 4.0 [b]	36.0 ± 4.0 [b]
$\lvert\mathcal{A}\rvert_{obs}$ (MHz)	76.7 ± 4.0	44.7 ± 6.8 [b]	31.9 ± 6.8 [b]
$\mathcal{A}_{calc}$ (MHz) [a]	81.0	51.0	34.2

[a] By simple hydrogenic theory of Ref. 12.
[b] Recalculated values from data of I (see Table III).

and triplet emission), we obtain for a final zero-field separation 20906 ±21 MHz. These results are summarized in Table III.

In I it was shown that the full widths at half-heights $\Delta\nu_c$ of the four anticrossings components could be written

$$\Delta\nu_c = 4|\mathcal{A}| f_M f_T, \tag{6}$$

where f_T has been defined by Eq. (4) and $\mathcal{A}$ is the off-diagonal spin-orbit coupling constant[1] between the $^{1,3}D$ states. The factor f_M equals $\sqrt{2}$ for the anticrossings involving the singlet $M_L = 2$ and -1 states and f_M equals $\sqrt{3}$ for the other two anti-crossings.[1] Using Descoubes's[9] measurements of $\tau_S = 61 \pm 6$ msec and $\tau_T = 82 \pm 8$ nsec for the $n = 6$ $^{1,3}D$ states we obtain $f_T = 1.01$. The observed lines for $n=6$, 7, and 8 were again fitted with a sum of four Lorentzians, but now weighted according to Table II. In this calculation the one variable parameter was $|\mathcal{A}| f_T$. The results are listed in Table IV.

V. CONCLUSIONS

The accuracy of the determination of the off-diagonal spin-orbit coupling constant $\mathcal{A}$ can be seen to increase as n decreases. Further, it is clear that there are no discrepancies between the observed value for any n and that calculated using a modification of the simple hydrogenic theory of Bethe and Salpeter.[12] This is somewhat surprising for $n=6$, where the experimental accuracy is highest and the theoretical prediction is expected to be worse.

The singlet-triplet separations, which are of course more accurately determined, do not yield to such a simple analysis. Indeed, the hydrogenic model predicts a zero separation. In Table V we combine our experimental results with the best theoretical calculations and previous optical observations. In comparing the optical singlet-triplet determinations with the anticrossing results we see that the new $n=6$ data, though more accurate, are in essential agreement with the earlier optical results. This result implies strongly the correctness of Herzberg's measurements[8] of the vacuum ultraviolet intercombination lines. The seemingly consistent deviation of the $n=7$ and 8 optical results from the anticrossing determination must now be assigned to small random measurement errors in the optical work which happened, coincidentally, to lead to the same inaccuracies for both the $n=7$ and 8 states.

Table V confirms our earlier observation, based only on the $n=7$ state, of the superiority in accuracy of the calculations of Poe and Chang[4-6] using many-body perturbation theory. For all three levels there is agreement between their calculation and our experimental results to within 200 MHz. Although more experimental results for different n would be required to be certain, the calculation's accuracy appears to be roughly independent of n, all calculated singlet-triplet intervals being slightly underestimated by the order of 100 MHz. Indeed, for those states (particularly high n, where intervals are small) where there are no experimental anticrossing or microwave data, we would presume that their calculated values[4-6,15] are more accurate than the experimental optical results.

TABLE V. Values (in GHz) of $^{1,3}D$ separations for $n=6$, 7, and 8 from theoretical calculations, optical measurements, and the present anticrossing experiments.

	Theoretical		Optical	Present
	Parish and Mires [a]	Poe and Chang [b]	Martin [c]	experiment
6*d*	65.7	20.82	20.8	20.91 ± 0.02
7*d*	42.8	13.56	14.7	13.63 ± 0.03
8*d*	29.3	9.28	10.8	9.47 ± 0.04

[a] R. M. Parish and R. W. Mires, Phys. Rev. A 4, 2145 (1971).
[b] Reference 6.
[c] Reference 7.

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[14]We note that with the nonunity weighting factors for the various anticrossings, the singlet and triplet anticrossing signals do not have to be centered at exactly the same magnetic field. However, in all observed states ($n=6$, 7, and 8) the difference in center position of the two anticrossings is predicted to be considerably less than the precision to which the line centers are quoted. Efforts to observe a difference in field positions for the $n=6$ ^1D and ^3D anticrossing yielded no significant result.
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