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Improved measurement of the ^{4}He I 3^1D-3^3D separation: Confirmation of predicted mass-polarization isotopic shift

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From new measurements of the ^{4}He $1s2p$-$1s3d$ lines, we have determined the 3^1D_2-3^3D_2 separation to be 102 459(15) MHz. The corresponding nonrelativistic $1s3d$ singlet-triplet separation is 102 196(15) MHz, as compared with the value 102 116(5) MHz previously determined for the equivalent ^{3}He separation. The difference of 80(16) MHz agrees with the predicted isotopic difference of these separations, the main contribution being a mass-polarization difference of 79 MHz as recently calculated by Drake. The experimental difference for $1s3d$ is consistent with the rough trend of such isotopic differences of $1snd$ singlet-triplet separations determined in previous experiments. We infer that mass-polarization shifts probably contribute significantly to the previously observed differences, at least up to $n \simeq 8$.

We have recently used a cw dye laser to measure the absolute wave numbers of the ^{4}He $1s2p$-$1s3d$ transitions in a low-pressure positive column discharge. The spin-allowed transitions were observed by Doppler-free intermodulated fluorescence spectroscopy[1] and the intercombination lines by Doppler-limited fluorescence spectroscopy. The dye laser wave number was measured relative to an iodine-stabilized He-Ne laser[2] by the classical method of photographic Fabry-Perot interferometry. Details of the experiment and complete results will be reported elsewhere. In this Communication we focus on the ^{4}He $1s3d$ singlet-triplet separation and discuss isotopic effects on the $1snd$ singlet-triplet intervals.

The wave numbers we measured for the two lines of interest here are 14 966.6522(5) cm^{-1} (2^1P_1-3^3D_2) and 14 970.069 85(9) cm^{-1} (2^1P_1-3^1D_2). The 3^1D_2-3^3D_2 separation is thus 102 459(15) MHz, as compared to the best previous values, 102 360(200) MHz (Ref. 3) and 102 499(300) MHz (Ref. 4).

We have used our new value for this separation, together with the experimental 3^3D fine-structure intervals,[5] to obtain an improved value for the nonrelativistic ^{4}He $1s3d$ singlet-triplet separation,[6] $E_0(3^1D)$-$E_0(3^3D)$, denoted here by $E_{st}(1s3d)$. The parameters $E_{st}(1snd)$, $\zeta_0(nd)$, and $\zeta_1(1snd)$ in the matrix of Bessis, Lefebvre-Brion, and Moser[6] were fitted to the three independent $1s3d$ level separations, the small $\zeta_2(1s3d)$ spin-spin interaction being fixed at the value[6] 14 MHz. The resulting parameter values were $E_{st} = 102\,196$ MHz, $\zeta_0 = 874$ MHz, and $\zeta_1 = 431.4$ MHz. As seen in Table I, the value for E_{st} is 80 MHz greater than the value obtained for this parameter in ^{3}He by Derouard, Lombardi, and Jost,[7] with a combined uncertainty of 16 MHz.

As defined here, the difference $E_{st}(1snd)$ is equal to the exchange separation,[8] $\frac{2}{5}G^2(1snd)$, plus the sum of any other significant contributions to the singlet-triplet separation not included in the matrix of Bessis, Lefebvre-Brion, and Moser.[6] The energy $\frac{2}{5}G^2(1s3d)$ is expected to be 4.6 MHz smaller for ^{3}He than for ^{4}He, due to the usual energy scaling by the reduced electron mass (the normal mass effect). This relatively small effect leaves an unexplained difference of 75.4(16.0) MHz between the $E_{st}(^4\text{He}\,1s3d)$ and $E_{st}(^3\text{He}\,1s3d)$ values.

Another source of isotopic shift is the mass-polarization energy ϵ_M arising from a term proportional to $\sum_{i<k} \vec{p}_i \cdot \vec{p}_k / M$ in the Hamiltonian, $\vec{p}_i$ and $\vec{p}_k$ being electron momenta and M the nuclear mass.[9] Assuming the difference of this energy for the 3^1D and 3^3D terms, $\epsilon_{Mst}(1s3d)$, to be significant we have

$$E_{st} = \tfrac{2}{5}G^2 + \epsilon_{Mst} \;;$$

and, if the difference in the ϵ_{Mst} values for ^{3}He and ^{4}He is to account for the above discrepancy,

$$\epsilon_{Mst}(^4\text{He}\,1s3d) - \epsilon_{Mst}(^3\text{He}\,1s3d) = 75.4 \text{ MHz} \;.$$

Since the ratio of the ϵ_M contributions to any separation in ^{3}He and ^{4}He, $\epsilon_M(^3\text{He})/\epsilon_M(^4\text{He})$, is equal to $M(^4\text{He})/M(^3\text{He}) = 1.327$, we obtain

$$\epsilon_{Mst}(^4\text{He}\,1s3d) = (-75.4/0.327) \text{ MHz} \;,$$

or $-231(49)$ MHz (the sign indicating a reduction of the singlet-triplet separation).

This result agrees very well with Drake's[10] recent calculation of the mass-polarization energies for the He $1s3d$ terms. He finds a downward shift of 216 MHz for the ^{4}He 3^1D level and an upward shift of only 23 MHz for the ^3D term, the corresponding shifts for ^{3}He being 287 and 31 MHz. The agreement of theory and experiment is shown

TABLE I. Frequencies corresponding to some energy differences and the exchange parameter for ^{4}He and ^{3}He $1s3d$. The nonrelativistic singlet-triplet separation, E_{st}, is obtained from the observed $1s3d$ level structure (including, for ^{3}He, the hyperfine structure). The exchange energy has been evaluated by assuming E_{st} to be the sum of the exchange separation $\frac{2}{5}G^2$ and a theoretical value for the mass-polarization contribution ϵ_{Mst}. Units are MHz.

	^{4}He	^{3}He
3^1D_2-3^3D_2	102 459(15)[a]	
$E_{st}(1s3d)$	102 196(15)[a]	102 116(5)[b]
$\epsilon_{Mst}(1s3d)$	−239[c]	−318[c]
$\frac{2}{5}G^2(1s3d)$	102 435	102 434

[a] Present results.
[b] Derouard, Lombardi, and Jost, Ref. 7.
[c] Values from Drakes's calculation, Ref. 10.

by comparison of Drake's value $\epsilon_{Mst}(^4\mathrm{He}\,1s3d) = -239$ MHz with the above value, −231(49) MHz, or equivalently, by comparison of the theoretical value

$$\epsilon_{Mst}(^4\mathrm{He}) - \epsilon_{Mst}(^3\mathrm{He}) = 79 \text{ MHz}$$

with the above result 75(16) MHz.

Bunge[11] has also calculated ϵ_M for ^{4}He 3^1D, obtaining a value equivalent to 230 MHz. His result combined with Drake's value of −23 MHz for the ^{4}He 3^3D shift gives

$$\epsilon_{Mst}(^4\mathrm{He}\,1s3d) = -253 \text{ MHz} \quad ,$$

also in agreement with experiment.

The values obtained for the integrals $\frac{2}{5}G^2(1s3d)$ by using the experimental $E_{st}(1s3d)$ values and Drake's ϵ_{Mst} values for ^{4}He and ^{3}He are also listed in Table I. The uncertainties of the values for $\frac{2}{5}G^2$ are omitted, since no estimate of the uncertainties of the calculated ϵ_M values are available. However, the good agreement noted above is here exhibited by the closeness of the difference of the two values of $\frac{2}{5}G^2$ (1 MHz) to the expected difference of 4.6 MHz.

Experimental differences between the ^{4}He and ^{3}He $1snd$ singlet-triplet separations, $\Delta E_{st}(^4\mathrm{He}\text{-}^3\mathrm{He})$, have also been determined for $n = 4$–8 (Refs. 7 and 12) and $n = 12$–17.[13] The ΔE_{st} results for $n = 4$ and 5 in Table II are from the ^{3}He measurements of Derouard, Lombardi, and Jost,[7] combined with ^{4}He data also obtained by anticrossing spectroscopy.[3,14] The ΔE_{st} values quoted for $n = 6$–8 are taken entirely from Panock *et al.*[12] in view of their belief that any systematic shifts of their measurements are equal for ^{3}He and ^{4}He. Bloomfield, Gerhardt, and Hänsch[13] determined the quoted ΔE_{st} values for $n = 12$–17.

The ΔE_{st} values for $n \geq 4$ in Table II have been regarded as anomalous and, in particular, too large to be explained by expected mass-dependent isotopic effects.[7,12,13] The normal-mass contributions to ΔE_{st} are relatively small (column headed "$\frac{2}{5}\Delta G^2$" in Table II) and can be omitted as insignificant for the accuracy of the data for higher n values. The quantities $\Delta E_{st} - \frac{2}{5}\Delta G^2$ (or ΔE_{st} for $n > 7$) remain to be accounted for.

Since no calculations of the $\epsilon_M(1snd)$ energies for $n \geq 4$ are available, one would like to estimate the ϵ_{Mst} values by scaling Drake's $1s3d$ result according to an appropriate n dependence. The relatively large ϵ_M shifts of the He $1snp$ terms[15] scale as n^{-3}, the predominant exchange contribution being proportional to the $1s$-np transition probability.[9] The mass-polarization energies for the other $1snl$ terms ($l \neq 1$) arise from correlation corrections due to electrostatic repulsion.[9] The calculated ϵ_M energies for the $1sns$ terms[15] also display an approximate n^{-3} dependence. An n^{-3} scaling of Drake's $1s3d$ $\Delta\epsilon_{Mst}$ result decreases too rapidly with n to fit the experimental data, however. In fact, as shown in the fifth column of Table II, an $n^{-3/2}$ dependence fits the data for $n = 3$–8 (fourth column) and for $n = 12$–17 (second column) to within the uncertainties.

Such a large deviation of the ϵ_M behavior from an n^{-3} dependence would be surprising and, in any case, other effects may well contribute to the $\Delta E_{st}(1snd)$ values. Isotopic differences in configuration interaction, for example, have been suggested as possible contributors.[7] As noted by Bloomfield, Gerhardt, and Hänsch,[13] any configuration-interaction effect on E_{st} in ^{3}He due mainly to hyperfine operators is expected to increase in relative importance with increasing n; their ΔE_{st} data for $n = 12$–17, in comparison with the trend for the lower configurations, is perhaps suggestive of such an effect. A crude approximation suggested

TABLE II. Differences ΔE_{st} between the ^{4}He and ^{3}He $1snd$ singlet-triplet separations. The quantity $\frac{2}{5}\Delta G^2$ is the expected (normal mass effect) difference of the exchange energies. The frequencies in the last two columns are explained in the text. All values in MHz.

n	ΔE_{st}	$\frac{2}{5}\Delta G^2$	$\Delta E_{st} - \frac{2}{5}\Delta G^2$	$79\left(\frac{3}{n}\right)^{3/2}$	$79\left(\frac{3}{n}\right)^{3} + 9$
3	80(16)[a]	4.6	75(16)	79	88
4	19(80)[b]	2.7	16(80)	51	42
5	40(17)[c]	1.5	39(17)	37	26
6	22(7)[d]	0.9	21(7)	28	19
7	20(7)[d]	0.6	19(7)	22	15
8	22(11)[d]	0.4	22(11)	18	13
12	9(7.5)[e]			9.9	10.2
13	5(5)[e]			8.8	10.0
14	13(7.5)[e]			7.8	9.8
15	10(15)[e]			7.1	9.6
16	16(15)[e]			6.4	9.5
17	20(15)[e]			5.9	9.4

[a] From Table I.
[b] Derouard, Lombardi, and Jost, Ref. 7.
[c] References 7 and 14.
[d] Panock *et al.*, Ref. 12.
[e] Bloomfield, Gerhardt, and Hänsch, Ref. 13.

by the data is an additional constant contribution to ΔE_{st}. As shown in the last column of Table II, a constant 9 MHz added to the $\Delta\epsilon_{Mst}$ values obtained by n^{-3} scaling fits the experimental ΔE_{st} data (any such constant from 6 to 9 MHz will fit these data).

Drake's calculation of $\epsilon_{Mst}(1s3d)$, as confirmed by experiment, leads us to conclude that mass-polarization shifts very probably contribute significantly to the other $1snd$ ΔE_{st} values, at least up to $n \simeq 8$. Calculations of the ϵ_M energies for $1snd$ ($n \geqslant 4$) terms are needed for critical comparison with the data, as are calculations of the isotopic differences in configuration-interaction effects. More accurate experimental determinations of the ΔE_{st} values can be expected, especially if new theoretical predictions become available.

Confirmation of the $1s3d$ mass-polarization shift has some pertinence to the recent measurements of the isotope shifts of the 2^3S-n^3D transitions ($n=3$–6) by de Clercq *et al.*[16] They compared the experimental shifts with theoretical values omitting mass-polarization contributions to the n^3D terms (no calculated values for these contributions being available to de Clercq *et al.*) but including calculated relativistic mass shifts of −10.9 or −11.0 MHz for each transition.[17] The difference between Drake's $\epsilon_M(3^3D)$ values for ^{4}He and ^{3}He is −7.7 MHz (with the sign convention of Ref. 16). If this difference is added to the net theoretical value obtained by de Clercq *et al.* for the 2^3S-3^3D isotopic shift, the result is 10.3 MHz less than the experimental shift of 37 480.4 MHz. Since the experimental uncertainty is ±7.0 MHz, some further refinement of the theoretical calculations may be indicated. The results of de Clercq *et al.* [without calculations of the $\epsilon_M(n^3D)$ energies] do not appear to constitute a definite verification of the calculated relativistic mass shifts.

The relatively large ϵ_M energies for the low He $1snp$ terms[15] are comparable in magnitude to the normal mass shifts $\epsilon_\mu(1snp)$ of the term values (ionization energies), whereas the ϵ_M shift for $1s3d\,^3D$ is smaller than $\epsilon_\mu(1s3d)$ by more than three orders of magnitude. The $\epsilon_{Mst}/\epsilon_{\mu st}$ ratios (relative contributions to the singlet-triplet *separations)* are, however, comparable for the $1snp$ and $1s3d$ configurations, the mass-polarization contribution being greater by an order of magnitude in each case (ratio of 17 for $1s3d$). The mass-polarization shift can thus be the dominant effect for relatively small separations of interest since the normal-mass effect scales down in proportion to the separation. The ϵ_M shift is very probably much the larger of the two effects for the other $1snd$ singlet-triplet separations of interest here.

Note added. After this paper was submitted for publication, we became aware of the calculations of ϵ_M for the ^{4}He I $1snl$ terms ($n=3$–12, $l=d,f,g$) by Cok and Lundeen.[18] Their results give a value of 93 MHz for the $1s3d$ $\Delta\epsilon_{Mst}(^4\text{He}$-$^3\text{He})$ difference, which is greater than the above value of 75(16) MHz for $(\Delta E_{st}-\frac{2}{5}\Delta G^2)$ by slightly more than the estimated experimental error. The n scaling of the first few $1snd$ $\Delta\epsilon_{Mst}$ values from these calculations varies from $n^{-1.9}$ to $n^{-2.5}$. The $\Delta\epsilon_{Mst}$ values for $n=4$–7 agree with the values of $(\Delta E_{st}-\frac{2}{5}\Delta G^2)$ (Table II) to within the errors of the latter. The calculated ϵ_M values for the $1snd\,^3D$ levels are small and behave irregularly, the resulting $\Delta\epsilon_M(^4\text{He}$-$^3\text{He})$ shifts for the $n=3,4,5,6$ ^3D levels being −7.0, −8.7, −5.8, and −3.8 MHz. Combination of these calculated shifts with the data for the isotopic shifts of the 2^3S-n^3D ($n=3$–6) transitions given by de Clercq *et al.*[16] yields a value of 2191.7(3.7) MHz for the specific mass shift of the 2^3S level (ϵ_M plus any relativistic mass shift). The quoted uncertainty includes only the experimental error, but this value now agrees with the value 2201.9(9.0) MHz recently obtained by Bloomfield, Gerhardt, and Hänsch,[19] to within the errors.

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