

Isotope shift of the thallium ($6s6p^2$) $^4P_{1/2}$ state

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We have measured the hyperfine splitting and level isotope shifts (LIS) of the ($6s6p^2$) $^4P_{1/2}$ level of ^{205}Tl and ^{203}Tl using laser absorption spectroscopy in a thallium oven near 1373 K. We determine that the hyperfine splitting between the $F=1$ and 0 levels of the $^4P_{1/2}$ state in ^{205}Tl is 75.179 ± 0.087 GHz. The $F=0$ LIS is -7.333 ± 0.025 GHz and the $F=1$ LIS is -6.500 ± 0.030 GHz, with the ^{205}Tl level below the ^{203}Tl level in both cases. We use our results together with other data to analyze the configuration mixing of the $^4P_{1/2}$ state with the nearby ($6s^210s$) $^2S_{1/2}$ state. The mixing inferred from the hyperfine results is consistent with that inferred from the isotope shift results.

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I. INTRODUCTION

The ground-state configuration of Tl I is $6s^26p$ and the excited levels are typically $6s^2nl$ by promotion of the ground-state $6p$ electron. In 1934, however, Buetler and Demeter [1] first identified several terms of the $6s6p^2$ configuration, namely the $^4P_{1/2}$, $^4P_{3/2}$, and $^2D_{3/2}$ where a closed-shell $6s$ electron is promoted instead. Of the $6s6p^2$ configuration terms, only $^4P_{1/2}$ lies below the ionization threshold of $49\,264\text{ cm}^{-1}$ and this state is the focus of our measurement. The excited-state hyperfine splitting of the ($6s^26p$) $^2P_{1/2}^o \rightarrow (6s6p^2)$ $^4P_{1/2}$ transition was first observed by Reeves and Garton [2] and estimated to be 84 GHz. Later Garton *et al.* were able to populate the upper fine-structure component of the ground state, ($6s^26p$) $^2P_{3/2}$, and observe the ($6s^26p$) $^2P_{3/2} \rightarrow (6s6p^2)$ $^4P_{1/2}$ transition at 267.18 nm ($37\,427.9\text{ cm}^{-1}$) [3,4], which is the same transition studied in this work. Additional ultraviolet spectroscopy on Tl I was done by Koslov and Krylov [5], who investigated many of the $6s6pnl$ levels which lie well above the ionization limit. In 1993, Hermann *et al.* [6] thoroughly studied the hyperfine splittings and isotope shifts of $n^2S_{1/2}$ with $n=7-12$ and the $n^2D_{3/2,5/2}$ levels for $n=6-10$ using an atomic beam and a frequency-doubled dye laser. The isotope shifts and hyperfine splittings of the ($7s$) $^2S_{1/2}$ were again measured as recently as 2000 [7] and now it is reasonable to say that the low-lying atomic level structure of Tl I is known to 25 MHz, and many measurements are better than 3 MHz.

However, the $6s6p^2$ terms have not been measured as precisely. These terms are interesting in part because they make a major contribution to the amplitude of parity nonconservation in Tl transitions [8]. Here we describe our measurement of the hyperfine structure and isotope shift of the bound term, the $^4P_{1/2}$ state, using the techniques of laser spectroscopy. We also examine the interesting perturbation generated

by the nearby ($6s^210s$) $^2S_{1/2}$ level. The anomalously large ($6s^210s$) $^2S_{1/2}$ isotope shift and hyperfine splitting is due to mixing with the ($6s6p^2$) $^4P_{1/2}$ wave function. We quantitatively characterize the extent of this mixing.

The relevant electronic structure of thallium is depicted in Fig. 1. In atoms with similar electronic structure to Tl I, namely Ga I, Al I, and In I, the $^4P_{1/2}$ state lies about $10\,000\text{ cm}^{-1}$ below ionization and about 2000 cm^{-1} from the nearest $6s^2nl$ term. In Tl, however, the $^4P_{1/2}$ state is barely bound while the $^4P_{3/2,5/2}$, $^2S_{1/2}$, $^2P_{3/2,1/2}$, and $^2D_{5/2,3/2}$ states are autoionizing. In addition, the Tl I $^4P_{1/2}$ state is observed to lie only 79 cm^{-1} from the ($6s^210s$) $^2S_{1/2}$ causing a strong perturbation in both levels. Apparently this perturbation was first noted by Beutler *et al.* [1] and more closely investigated by Hermann *et al.* [6], who measured an anomalously large ($6s^210s$) $^2S_{1/2}$ hyperfine splitting of $20.9409\text{ GHz} \pm 9.9\text{ MHz}$ in ^{203}Tl and $21.0160\text{ GHz} \pm 3.5\text{ MHz}$ in ^{205}Tl . This splitting exceeds by a factor of 12 the expected hyperfine splitting trend of the $n^2S_{1/2}$ terms [which normally goes as $(n^*)^{-3}$, where n^* is the effective quantum number]. This large splitting is due to configuration

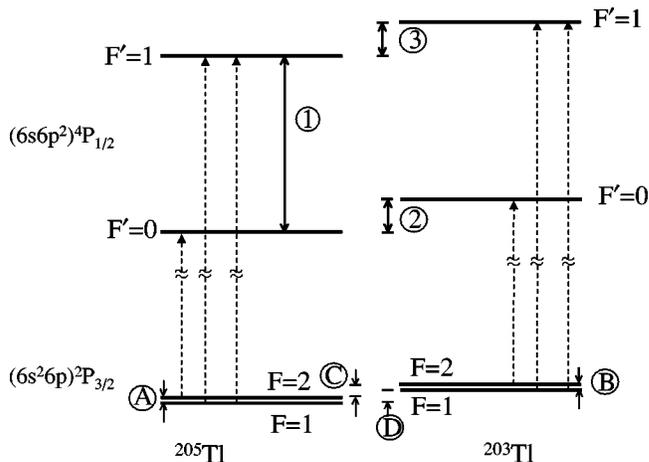


FIG. 1. Details of the $6s^26p^2$ $^2P_{3/2} \rightarrow 6s6p^2$ $^4P_{1/2}$ transition in the stable isotopes of thallium. The measurements reported in this paper are labeled (1), (2), and (3). Their values are presented in Table I. Previous measurements are labeled (A), (B), (C), and (D) and can also be found in Table I.

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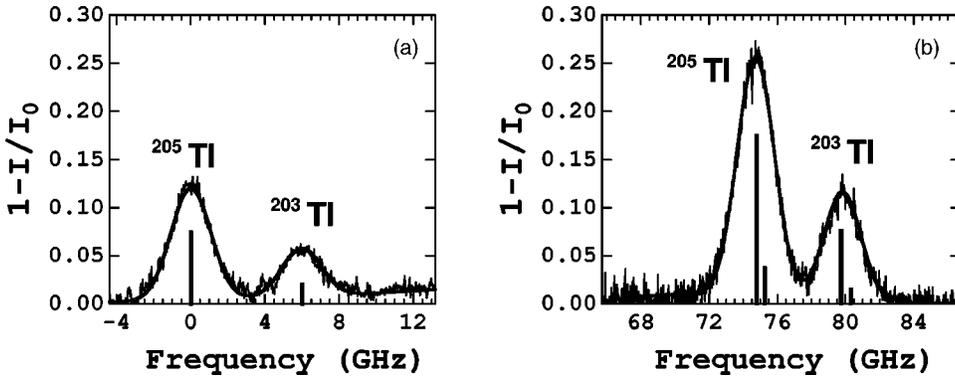


FIG. 2. Representative scans of the observed Doppler broadened line shapes of the $6s6p^2$ $^4P_{1/2}$ term. (a) $F' = 0$. (b) $F' = 1$. The vertical lines represent the approximate position of the transition centers. The frequency scale is referenced to the ^{205}Tl $F = 1$ to $F' = 0$ transition.

mixing with the nearby $(6s6p^2)$ $^4P_{1/2}$ state, which has a very large hyperfine splitting. (Configuration mixing between a $^2S_{1/2}$ state and a $^4P_{1/2}$ state with different nominal values of L and S is not surprising in a heavy element like thallium due to the breakdown of LS coupling [8].) The extent of $(6s^210s)$ $^2S_{1/2} - (6s6p^2)$ $^4P_{1/2}$ mixing may be calculated from measurements of the state hyperfine splittings [9], as we do below, and this mixing can be used to interpret our isotope shift measurements.

In addition, the best calculations of parity nonconservation in thallium [10,11] are validated by predicting fine and hyperfine splittings, term energies, and transition amplitudes for various levels. Better measurements of the $^4P_{1/2}$ level hyperfine splitting and isotope shift may help reduce the error bars on future calculations.

II. EXPERIMENTAL METHOD

A ring dye laser (Coherent 699) running with PM 556 dye provides 150–300 mW of output power at 534 nm. This light is passed through a nonlinear crystal (BBO-cut for 486.28 nm) yielding about 0.6 μW of frequency-doubled laser light at 267 nm. This ultraviolet light is routed to a ceramic thallium oven operated between 1073 and 1373 K. The ultraviolet light transmitted through the oven is detected on a solar blind photomultiplier tube which rejects the glow of the oven wall. The phototube signal is normalized against a sample of the probe light that does not pass through the oven. No attempt is made to achieve a Doppler free signal.

The transition we investigate is $(6s^26p)$ $^2P_{3/2} \rightarrow (6s6p^2)$ $^4P_{1/2}$. The Tl I ground state, $(6s^26p)$ $^2P_{1/2}$, is 7792.7 cm^{-1} below $^2P_{3/2}$ and the relative proportion of atoms in the $^2P_{3/2}$ state is 74.7×10^{-6} at 1100 K and 671×10^{-6} at 1400 K. The vapor pressure is expected to be 48 Torr at 1400 K implying a $^2P_{3/2}$ number density of $10^{13}/\text{cm}^3$. Most of our data are taken under these conditions.

The laser is initially positioned near the resonance using a wavemeter (Burleigh WA-20 DL) and the laser is scanned until the absorption signal is observed. Due to the limited 30 GHz scanning range of the laser it was not possible to continuously scan over both hyperfine components of the transition. Therefore, one sample of the undoubled 534-nm beam is routed to a 300.8-MHz FSR reference cavity and another to an iodine cell. The cavity fringes and the molecular iodine absorption signal provide redundant markers that allow us to blend the scans together [12,13].

III. MEASUREMENTS AND RESULTS

The data on the $(6s^26p)$ $^2P_{3/2} \rightarrow (6s6p^2)$ $^4P_{1/2}$ transition are presented in Fig. 2. Two pairs of Doppler-broadened peaks are evident. The pair on the left is assigned to $F = 1 \rightarrow F' = 0$ and the set on the right is assigned to the $F = 1, 2 \rightarrow F' = 1$. Here the prime indicates the $^4P_{1/2}$ hyperfine states. The larger peak of each pair is associated with ^{205}Tl (70.476% abundance) and the smaller peak ^{203}Tl (20.524% abundance). The hyperfine splitting of $(6s^26p)$ $^2P_{3/2}$ is 530 MHz (^{205}Tl) and 524 MHz (^{203}Tl) and is not resolved in the rightmost pair. There is no lower-state hyperfine splitting embedded in the leftmost pair and therefore we require two separate line-shape models. In the $F' = 1$ model the $F = 2 \rightarrow F' = 1$ transition rate is five times greater than the $F = 1 \rightarrow F' = 1$. The adjustable parameters in the model are the Doppler width, two transition isotope shifts, the hyperfine splitting, the absorption depth, and a cubic fit for the line-shape baseline.

Errors come from two sources: the scan calibration and the line-shape model. These two sources make roughly equal contributions to the total error of both the hyperfine splitting and the isotope shift measurements. Our absorption scan is calibrated against the 300.8-MHz reference cavity. The free spectral range of the cavity is calibrated against the known hyperfine splitting of the H_{6s^210s} $^2S_{1/2}$ and we estimate the error of this calibration to be 0.11%. Our final measurement results and error estimates are presented in Table I.

IV. DISCUSSION

We are now in a position to calculate the mixing between the $^4P_{1/2}$ and the nearby $(6s^210s)$ $^2S_{1/2}$ caused by the perturbation mentioned in the Introduction. This was first done by Flambaum and Sushkov [9] using the measurements of Garton *et al.* [4]. The level energy, hyperfine splitting, and isotope shift for the $6s^2ns$ states do not show a significant departure from expected trends except in the case of $6s^210s$. A detailed analysis of these trends shows that the off-diagonal matrix element mixing the $6s^2ns$ and $6s6p^2$ configurations must be much less than all relevant energy intervals except the one anomalously small interval between the $(6s^210s)$ $^2S_{1/2}$ and $^4P_{1/2}$ states. We therefore assume, as was done in [9], a coupled system of just two states, $(6s6p^2)$ $^4P_{1/2}$ and $(6s^210s)$ $^2S_{1/2}$.

We define the mixing parameter ϵ by

TABLE I. Our measurements of the ($6s^26p$) $^2P_{3/2} \rightarrow (6s6p^2)$ $^4P_{1/2}$ hyperfine splitting and ($6s6p^2$) $^4P_{1/2}$ LIS. Also included are some additional splittings relevant to Fig. 1.

Measurement	Fig. 1 label	Value (GHz)	Previous measurements
^{205}Tl $6s6p^2$ $^4P_{1/2}$ hyperfine splitting	1	75.179 ± 0.087	75.218 ± 0.180 [4]
$6s6p^2$ $^4P_{1/2}$ $F=0$ LIS	2	-7.333 ± 0.025	7.49 ± 0.45
$6s6p^2$ $^4P_{1/2}$ $F=1$ LIS	3	-6.500 ± 0.030	6.32 ± 0.45
^{205}Tl $6s^26p$ $^2P_{3/2}$ hyperfine splitting	A	0.530	[6]
^{203}Tl $6s^26p$ $^2P_{3/2}$ hyperfine splitting	B	0.524	[6]
$6s^26p$ $^2P_{3/2}$ $F=2$ LIS	C	-1.354	[6]
$6s^26p$ $^2P_{3/2}$ $F=1$ LIS	D	-1.360	[6]

$$|(10s) \ ^2S'_{1/2}\rangle = N[|(10s) \ ^2S_{1/2}\rangle + \epsilon|(6s6p^2) \ ^4P_{1/2}\rangle],$$

$$|(6s6p^2) \ ^4P'_{1/2}\rangle = N[|(6s6p^2) \ ^4P_{1/2}\rangle - \epsilon|(10s) \ ^2S_{1/2}\rangle].$$

The unprimed states are central field states in intermediate coupling, designated by their nominal LS values. (These states are linear combinations of true LS states of the same configuration; e.g., what is called $^4P_{1/2}$ is actually a mixture of $^4P_{1/2}$, $^2P_{1/2}$, and $^2S_{1/2}$.) The primed states are the spectroscopic states that include configuration mixing by noncentral electron-electron forces. The normalization factor $N = 1/\sqrt{1+\epsilon^2}$ [14].

To find the value of ϵ , we first use the known hyperfine splittings (from [6]) of the ($6s^2ns$) $^2S_{1/2}$ states for $n \neq 10$, scaled by $1/(n^*)^3$, to find the unperturbed hyperfine splitting of the ($6s^210s$) $^2S_{1/2}$ state. We obtain 0.893 ± 0.15 GHz for ^{205}Tl and 0.885 ± 0.15 GHz for ^{203}Tl . The scatter about the trend with n^* contributes an uncertainty of 0.15 GHz to these numbers. Next we use the measured ($6s^210s$) $^2S_{1/2}$ splitting (also from [6]) and our ($6s6p^2$) $^4P_{1/2}$ hyperfine splitting measurement to calculate ϵ , which yields $|\epsilon| = 0.530$ for ^{205}Tl and $|\epsilon| = 0.522$ for ^{203}Tl . The previous treatment [9] yields $|\epsilon| = 0.53$ for both isotopes. The errors in the hyperfine splittings and the $1/(n^*)^3$ trend contribute an uncertainty of less than 0.01 to the value of ϵ . However, to place reliable overall error bars on ϵ would require a better estimate of the accuracy of the quantum defect method than we have made.

This mixing not only adds to the hyperfine splitting of the ($6s^210s$) $^2S_{1/2}$ state, but will boost the isotope shift as well. The measured isotope shift of the $6s^2ns$ $^2S_{1/2}$ series starts at

407.3 MHz for $n=7$ and, except for $n=10$, it smoothly declines to 11.7 MHz for $n=12$. However, Ref. [6] reports the $6s^210s$ $^2S_{1/2}$ LIS to be -1930.3 ± 3.6 MHz (the LIS is negative when the ^{205}Tl level lies below the ^{203}Tl level), a clear deviation from this trend and evidence of perturbation. Based on the trend established by the (presumably unperturbed) $6s^2ns$ ($n=7-12$, $n \neq 10$) isotope shifts we expect the LIS of the $6s^210s$ state to be $+26 \pm 7$ MHz. We assume that the large observed ($6s^210s$) $^2S_{1/2}$ LIS is due mostly to the $^4P_{1/2}$ admixing caused by the configuration interaction, just as with the large $6s^210s$ hyperfine structure, and that we can estimate the expected isotope shift using the value of ϵ found by our measurement of hyperfine structure. Using the isotope-averaged value of $\epsilon = 0.522$ we calculate an expected isotope shift of -1.805 GHz. This differs by 6.5% from the measured LIS of the $6s^210s$ $^2S_{1/2}$ level of -1.9303 GHz [6].

V. FUTURE DIRECTIONS

In addition to its interest in connection with atomic parity nonconservation, thallium is a common testing ground for many-body atomic physics calculations; future *ab initio* work will be challenged to achieve consistency with our measurement. This experiment was done in a Doppler-broadened environment, but the accuracy should be adequate for theoretical investigations in the near future. If accuracy ever does become an issue, there is no particular obstacle to executing this measurement in an atomic beam with more precise calibration techniques.

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[1] H. Beutler and W. Demeter, Z. Phys. **91**, 143 (1934).
 [2] E. M. Reeves, W. R. S. Garton, and A. Bass, Proc. Phys. Soc. London **86**, 1077 (1965).
 [3] W. R. S. Garton, W. H. Parkinson, and E. M. Reeves, Can. J. Phys. **44**, 1745 (1966).
 [4] W. R. S. Garton, E. M. Reeves, and F. S. Tomkins, Proc. R. Soc. London, Ser. A **341**, 163 (1974).
 [5] M. G. Koslov and B. E. Krylov, Opt. Spectrosc. **38**, 471 (1975).

[6] G. Hermann, G. Lasnitschka, and D. Spengler, Z. Phys. D: At., Mol. Clusters **28**, 127 (1993).
 [7] D. S. Richardson, R. N. Lyman, and P. K. Majumder, Phys. Rev. A **62**, 012510 (2000).
 [8] V. N. Novikov, O. P. Sushkov, and I. B. Khriplovich, Sov. Phys. JETP **44**, 872 (1976).
 [9] V. V. Flambaum and O. P. Sushkov, J. Quant. Spectrosc. Radiat. Transf. **20**, 569 (1978).
 [10] V. A. Dzuba, V. V. Flambaum, P. G. Silvestrov, and O. P. Sus-

- hkov, J. Phys. B **20**, 3297 (1987).
- [11] M. G. Koslov, S. G. Porsev, and W. R. Johnson, Phys. Rev. A **64**, 052107 (2002).
- [12] S. Gerstenkorn and P. Luc, *Atlas du Spectre d'Absorption de la Molecule d'Iode* (Centre National de la Recherche Scientifique, Paris, 1978).
- [13] S. Gerstenkorn and P. Luc, Rev. Phys. Appl. **14**, 791 (1979).
- [14] Reference [9] defines the mixing parameter differently. There $|(6s6p^2) \ ^4P'_{1/2}\rangle = \sqrt{1-\beta^2} [|(6s6p^2) \ ^4P_{1/2}\rangle + \beta |(10s) \ ^2S_{1/2}\rangle]$. The connection is $\beta = \epsilon/\sqrt{1+\epsilon^2}$.