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Measurement of the $4s4p\ ^1P-4s3d\ ^1D$ spontaneous emission rate in calcium by use of a Stark–electric-quadrupole interference

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An interference between electric quadrupole and Stark-induced dipole amplitudes is observed for the first time in calcium. From our measurement of the atomic polarization produced by this interference we obtain $A(4s4p\ ^1P-4s3d\ ^1D)=(3.68\pm0.89\pm0.11)\times10^3\ s^{-1}$. This result suggests that the laser cooling of atomic calcium is feasible.

The intercombination lines of calcium have been considered possible optical frequency standards. For that reason, various research groups have expressed interest in being able to laser-cool neutral calcium through multiple laser excitation of the $4s^2\ ^1S$ to $4s4p\ ^1P$ transition.[1] The feasibility of such an enterprise depends on the branching of the $4s4p\ ^1P$ state to the metastable $4s3d\ ^1D$ level. Excited atoms, which decay to the $4s3d\ ^1D$ level instead of to the ground $4s^2\ ^1S$ state, fall out of resonance with the cooling beam and are lost as far as laser cooling is concerned. Calcium atoms emerging in a beam from a 1000-K oven will require, on the average, 4×10^4 photon absorptions without a transition to the ^1D state in order to be brought to rest. For efficient cooling, the branching ratio in question must therefore be less than about 2.5×10^{-5}, or the A coefficient $A(4s4p\ ^1P-4s3d\ ^1D)$ must be less than about $5.5\times10^3\ s^{-1}$, since $A(4s4p\ ^1P-4s^2\ ^1S)=2.18\times10^8\ s^{-1}$.[2]

In addition to determining whether calcium can be laser-cooled efficiently, an accurate value for $A(4s4p\ ^1P-4s3d\ ^1D)$ is required for a good quantitative test of the theory of pair absorption in calcium.[3] Without this value, the results of the pair absorption experiment of Ref. 3 can at best be combined with two experiments in barium to yield a limit on $A(4s4p\ ^1P-4s3d\ ^1D)$.

Present theoretical values for $A(4s4p\ ^1P-4s3d\ ^1D)$ differ by over two orders of magnitude due to a near cancellation between the contributions of different electronic configurations to the relevant transition matrix element.[4–8] The result reported in the present paper is the first actual measurement of the rate. The measurement was made using Stark–electric-quadrupole interference, a technique recently developed and successfully applied to determine the $A(5s5p\ ^1P-5s4d\ ^1D)$ decay rate in strontium.[9]

Since the technique is described at length in Ref. 9, we only briefly outline it here. A small, uniform electric field, directed along **y**, is applied to the calcium sample, Stark mixing the original eigenstates of the unperturbed Hamiltonian. A forbidden quadrupole transition from the perturbed $4s^2\ ^1S$ state to the perturbed $4s3d\ ^1D$ level is then excited with 458-nm light propagating along **x**. The amplitude of the corresponding transition matrix is the usual electric quadrupole amplitude Q, plus a Stark-induced electric dipole amplitude S. The latter is dominated by the $4s^2\ ^1S$ to $4s4p\ ^1P$ transition term, for the main contribution to the perturbation of the $4s3d\ ^1D$ state is the mixing of the $4s4p\ ^1P$ level that is only 1802 cm^{-1} away. The coefficient of this dominant term is proportional to $[A(4s4p\ ^1P-4s3d\ ^1D)]^{1/2}$.

Solving the angular integrals involved in the expressions for S and Q yields the relative transition probabilities to the various magnetic sublevels of the ^1D state shown in Fig. 1. Although the interference terms between the quadrupole and Stark amplitudes cancel in the total intensity, they induce an asymmetry in the populations of the $4s3d\ ^1D$ state's magnetic sublevels (i.e., a polarization) which is proportional to S. Because the $4s3d\ ^1D$ level is metastable, the atoms will depolarize long before fluorescing through collisions and the precession of their angular momentum vectors about small, stray magnetic fields. To remedy this problem, we immediately excite the atoms to $4p3d\ ^1F$ with an analyzing beam at 535 nm propagating along **x**. If the analyzing beam is polarized along **z**, the asymmetry of the ^1D state is transfered unchanged to the ^1F level. The resulting asymmetry in the circular polarization of the fluorescence, defined to be the difference in the number of fluorescent photons which have plus or minus one unit of angular momentum along the z axis di-

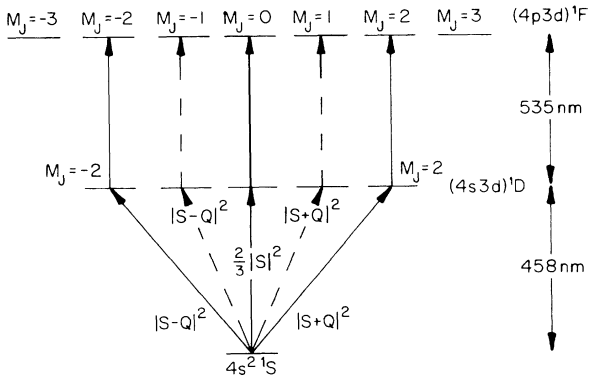

FIG. 1. Relative excitation probabilities for the various magnetic sublevels. S and Q represent the Stark and quadrupole amplitudes. The solid (dashed) lines represent the transitions corresponding to a pump beam polarized along **y** (**z**). In both cases, the analyzing beam is polarized along **z**.

vided by the total number of detected photons, is

$$A_{\text{fluo}}=\frac{4KceE}{\hbar R_{DS}\omega_{DS}^2}\sum_{^1P}(R_{nPS}R_{DnP})\left(\frac{\omega_{DnP}}{\omega_{SnP}}-\frac{\omega_{SnP}}{\omega_{DnP}}\right), \quad (1)$$

where we have used the fact that the Stark contribution is much smaller than that of the quadrupole term for the electric field strengths used in this experiment. Here, K equals 1 when the light that pumps the forbidden quadrupole transition is polarized along **y** and $\frac{5}{7}$ when it is polarized along **z**. The sum is over all ^1P states. R_{ab} is the relevant radial matrix element between states a and b as defined in Ref. 9, and ω_{ab} is the angular frequency separation between these states. We note that R_{DS} has the dimension of length squared, while the other radial matrix elements have the dimension of length. E is the magnitude of the electric field, e the charge of the electron, and c the speed of light.

Experimentally, it is the above asymmetry that we measure. To determine the apparatus' efficiency for detecting this asymmetry, we create a known asymmetry in the populations of the ^1D state's magnetic sublevels. This calibration asymmetry is produced by applying a magnetic field of magnitude 18.9 ± 0.1 G along **z** and tuning the 458 nm laser to the side of the atomic resonance, thereby preferentially exciting one of the Zeeman-shifted magnetic sublevels. From a knowledge of the quadrupole transition's absorption profile $I(\nu)$ one can predict how large this Zeeman-induced circular polarization asymmetry should be:

$$A_{\text{expected}}=K\left(\frac{I(\nu_b-C\mu_0B/h)-I(\nu_b+C\mu_0B/h)}{I(\nu_b-C\mu_0B/h)+I(\nu_b+C\mu_0B/h)}\right),$$

where ν_b is the frequency at which the laser is detuned. Here, $C=2$ when the 458 nm light is polarized along **y** and $C=1$ when it is polarized along **z**.

By methods described later in the paper, the 458 nm laser was found to be well approximated by a Lorentzian profile of width [full width at half maximum (FWHM)] $\Delta\nu_L=3.6\pm0.2$ GHz. The absorption profile is therefore a Voigt curve, the convolution of the laser's Lorentzian profile with the transition's Gaussian frequency distribution:

$$I(\nu_1)\propto\int_0^{+\infty}\frac{\exp\{[2(\ln2)^{1/2}(\nu-\nu_0)]/\Delta\nu_D\}^2}{1+4[(\nu-\nu_1)/\Delta\nu_L]^2}d\nu,$$

where $\Delta\nu_D=2.18$ GHz is the Doppler width (FWHM) of the quadrupole transition for a cell temperature of 860 K, ν_1 is the frequency at which the laser is tuned, and ν_0 the quadrupole transition frequency. A fit of the observed calcium absorption scan in zero magnetic field to the anticipated Voigt profile is shown in Fig. 2.

The 458 nm quadrupole transition is excited by a transversely pumped dye laser. The nitrogen pump has a (4 ± 1)-ns pulse with an energy of 2 to 3 mJ. A 2.5 mm, 85% reflecting étalon (Burleigh model FG-6), and an 1800 lines/mm diffraction grating with a 340 nm blaze (Instruments SA) define the laser frequency. A telescope (Oriel, ×40) is used to expand the beam to the dimensions of the tuning elements. With a single-stage amplifier, the dye laser output is typically 80 μJ per pulse.

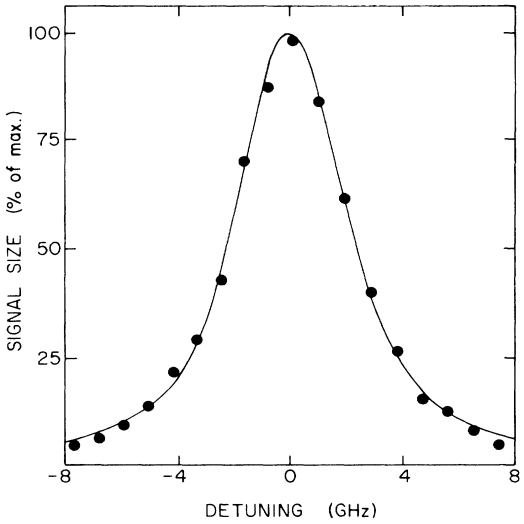

FIG. 2. Voigt fit of the $4s^2\ ^1S-4s3d\ ^1D$ transition in atomic calcium.

The laser's profile and bandwidth were determined using the cesium ground-state hyperfine structure. The technique consists in scanning the laser across the two transitions from the $6\ ^2S_{1/2}$ ground state to either the $7\ ^2P_{1/2}$ or $7\ ^2P_{3/2}$ states. These two transitions, whose respective resonant wavelengths are 459 and 456 nm, nicely flank the 458-nm calcium quadrupole transition, making it possible to test the laser's behavior over a range of wavelengths centered at the wavelength at which the experiment is performed.

Each line was scanned over a range of 20 GHz, and the intensity of the 852 nm cascade fluorescence was recorded. The data for each fine-structure transition are well fitted by a pair of Lorentzians, strongly suggesting that the laser's profile, which is the main contribution to this absorption profile, is also Lorentzian (Fig. 3). The known

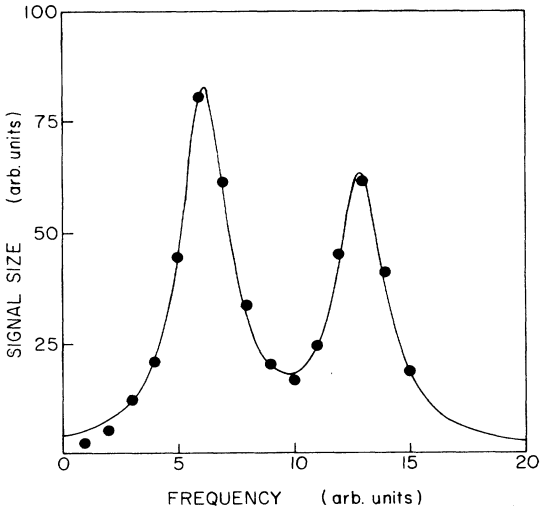

FIG. 3. Lorentzian fit of the cesium $6^2S_{1/2}-7\ ^2P_{3/2}$ absorption profile.

separation of the two ground-state hyperfine components ($F=3$ and $F=4$) (Ref. 10) served as a means of calibrating the frequency axis of the fit plots. The averaging of the deduced laser widths measured before and after the actual experiment yields a Lorentzian laser width $\Delta\nu_L=(3.6\pm0.2)$ GHz. This average value includes a correction for a cesium Doppler width of 773 MHz. The result is consistent with width measurements made with a Fabry-Perot spectrum analyzer.

The 535-nm analyzing transition is excited by a flashlamp pumped dye laser that typically outputs 0.22 mJ in a 500-ns pulse. The output was attenuated by a factor of about 10 to optimize the experimental signal to noise. The dominant background contribution, which is associated with scattered 535-nm light, was usually less than 5% of the signal. The other laboratory instruments, the basic operating parameters, and the experimental procedure are essentially those described in Ref. 9. A total of four days of data are included here. The results are summarized in Table I. The polarization of the ^1D state is found to be positive along **z** when **E** is along **+y** and **k** is along **+x**. As predicted by theory, the measured asymmetry changes sign as the propagation direction of the 458 nm beam is reversed. The data are also consistent with the prediction that the asymmetry, resulting from a geometry in which **e** is parallel to the z axis, should be $\frac{5}{7}$ of the asymmetry produced by light polarized along **y**.

Once the appropriate factors of $\frac{5}{7}$ and sign changes have been taken into account, the normalized data from these four days agree within the quoted experimental uncertainties and may be combined. The results are shown in Fig. 4, where the combined, measured, and normalized asymmetry (i.e., the polarization of the ^1D state) is plotted versus the potential difference applied to the cell's electrodes. The slope and the intercept associated with the best-fit line are, respectively, $(3.87\pm0.14)\times10^{-5}$ V^{-1} and $(-0.24\pm0.37)\times10^{-3}$. We note that the intercept is consistent with zero: when no field is applied, there is no Stark mixing of the atoms' states and, therefore, no interference and no asymmetry.

A value for the spontaneous decay rate $A(4s4p\,^1P\text{–}4s3d\,^1D)$ can be deduced from the above slope through an equation which is derived from Eq. (1) and from expressions relating the radial matrix elements R_{nPS}, R_{DnP}, and R_{DS} to their corresponding A coefficients (Ref. 9). We find, assuming that the entire measured asymmetry is due to the mixing of the $4s4p\,^1P_1$ level,

$$A(4s4p\,^1P\text{–}4s3d\,^1D)=(4.32\pm1.05\pm0.96)\times10^3\ s^{-1}\ .$$

The first uncertainty is the combination of the one standard deviation, uncertainty in our measured asymmetry with the uncertainties associated with the various other experimental parameters used to deduce $A(4s4p\,^1P\text{–}4s3d\,^1D)$. The main contribution to this uncertainty is the 20% uncertainty associated with the measurement[11] of $A(4s3d\,^1D\text{–}4s^2\,^1S)=(40\pm8)\ s^{-1}$. The second uncertainty represents the maximum modification the Stark interference associated with higher ^1P levels ($n>5$) could produce in our result.

This second uncertainty is deduced making the conservation assumption that all of the higher ^1P levels have the same sign of the relevant radial matrix elements, but allow that this sign may be the same as or opposite to the dominant $(4s4p)\,^1P$ term. The values for the $4snp\,^1P$ to $4s^2\,^1S$ oscillator strengths ($n<17$) used to determine the magnitudes of the various radial matrix elements, are those of Ref. 2. $A(4snp\,^1P\text{–}4s3d\,^1D)$, $n=5$ and 6 are taken from Ref. 12, while $n=7$ and 8 are from Ref. 5. For larger n, we assumed that the relevant A coefficients continue to fall off with the anticipated $1/n^3$ dependence.

A better estimate of $A(4s4p\,^1P\text{–}4s3d\,^1D)$ can be obtained if the signs of the various radial matrix elements are known. The signs for the radial matrix elements R_{nPS} and R_{DnP} with $n<9$ have been generously provided by George Victor. He predicts that all of these radial matrix elements are positive except for R_{D5P}. With these signs taken into account, our result becomes

$$A(4s4p\,^1P\text{–}4s3d\,^1D)=(3.68\pm0.89\pm0.11)\times10^3\ s^{-1}\ .$$

In Table II, we list theoretical and experimental estimates of $A(4s4p\,^1P\text{–}4s3d\,^1D)$. The experimental limits from Ref. 3 have been corrected to include the most recent measurement of $A(6s6p\,^1P\text{–}6s5d\,^1D)$ in barium.[13] Our result suggests that the laser cooling of neutral calcium is feasible.

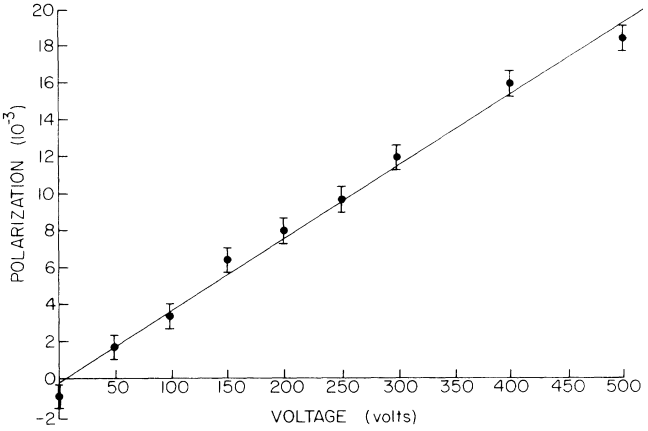

FIG. 4. The normalized polarization of the ^1D state as a function of applied voltage. The electrode separation is 6.96 mm.

TABLE I. Results of an independent analysis of each days data. **k** is the propagation direction of the beam that pumps the quadrupole transition and **e** is its linear polarization direction. The analyzing power is defined to be the observed Zeeman induced circular polarization asymmetry divided by A_{expected}. A_{fluo} has been corrected for the analyzing power.

k	**e**	Analyzing power (%)	A_{fluo} (%/kV)
$+x$	y	78.3 ± 4.7	3.48 ± 0.35
$+x$	z	64.1 ± 10.7	2.40 ± 0.47
$-x$	y	82.1 ± 4.7	-3.47 ± 0.36
$-x$	y	84.4 ± 2.4	-4.15 ± 0.18

TABLE II. Calculated (T) and experimental (E) values for the calcium $4s4p\ ^1P-4s3d\ ^1D$ A coefficient.

$A(4s4p\ ^1P-4s3d\ ^1D)$ (s^{-1})	Method	Reference
4.6×10^4	T(velocity representation)	4
4.67×10^3	T	5
3.5×10^3	T(length representation)	4
2.3×10^3	T	6
7.8×10^2	T	7
2.3×10^2	T	8
$(0.2-6)\times10^3$	E	3
$(3.68\pm0.89\pm0.11)\times10^3$	E	Present result

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