Measurement of the Fine-Structure Splitting of the 4F State in Atomic Sodium Using Two-Photon Spectroscopy with a Resonant Intermediate State

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The fine-structure splitting of the $4F$ state of atomic sodium is determined using the technique of two-photon spectroscopy with a resonant intermediate state. The sensitivity of this Doppler-free technique allows observation of the electric-dipole–forbidden $3S \rightarrow 4F$ two-photon transition. The $4F$ fine-structure splitting is found to be 229 ± 4 MHz. Its sign and magnitude are hydrogenic, in complete contrast to the D levels of Na.

Recently, new techniques using tunable lasers have allowed high-resolution measurements to be made of atomic states which are not directly coupled to the ground state via an electric-dipole matrix element. With Doppler-free two-photon spectroscopy[1] it has been possible to measure fine and hyperfine structure in the S and D states of alkali metal vapors. Other methods which have been used combine stepwise excitation of an atom by tunable dye lasers with level-crossing techniques,[2] optical double resonance,[2] or quantum beat spectroscopy.[3] These measurements have yielded a great deal of information about these states. In this Letter, we report the first measurement of the fine-structure splitting of the $4F$ state of atomic sodium. This measurement was made using the technique of two-photon spectroscopy with a resonant intermediate state. The technique gives Doppler-free spectra even though unequal-frequency photons are used. It also maximizes the two-photon transition rate, which makes it possible to observe the weak electric-dipole–forbidden $3S \rightarrow 4F$ two-photon transition. This transition can occur because of electric-quadrupole coupling between the $4F$ state and the $3P$ intermediate state.

The fine-structure splitting in alkali atoms is quite interesting. It is well known that in many of the alkalis the fine structure of the D doublets is inverted (the state with $J = L + \frac{1}{2}$ has lower energy than the state $J = L - \frac{1}{2}$). In Rb the lowest-lying D level is inverted[4] while the higher D states have a normal order.[5] In sodium all the D states which have been measured, even highly excited D states up to $n = 16$, are inverted.[3] Recently Gallagher, Hill, and Edelstein have induced microwave transitions from laser-excited D states to F states in sodium and have determined the fine-structure splitting of some highly excited ($n = 11$ to 17) F states.[6] The fine-structure interval of these states was found not to be inverted; however, earlier measurements[5,7] had found that the lowest-lying F states in the alkali atoms, Rb and Cs, are inverted. Our measurement of the lowest-lying F state in sodium shows that this level is similar to the highly excited F levels in that this interval is not inverted. Combining our result with those of Ref. 6, we find that in sodium the magnitude of the F-state fine-structure splitting, its sign, and its dependence on the principal quantum number, n, are hydrogenic in nature.

Two-photon spectroscopy is generally restricted to those levels which are of the same parity as the ground state, and which have allowed electric-dipole transitions to intermediate states that are connected to the ground state also via an electric-dipole transition. Two-photon transitions from the $3S$ ground state to the $4F$ state in sodium are therefore forbidden to first order. However, transitions can be induced by way of electric-quadrupole matrix elements which connect the $4F$ state with intermediate states. These matrix elements have recently been shown to contribute importantly to multiphoton ionization processes.[8] The transitions are $\sim 10^{-6}$ weaker than electric-dipole–allowed two-photon transitions, and therefore might be expected to be detected only with great difficulty. The two-photon transition rate can be increased by using two unequal-frequency photons (ν_1 and ν_2) and tuning the frequency ν_2 to be resonant with the ground-to-intermediate-state transition. In recent experiments[9] we have shown that the enhancement produced by the resonant intermediate state can increase the transition rate by nearly 10 orders of magnitude so that the weak quadrupole transition should be easily observable.

Unlike the case of equal-frequency photons, when unequal-frequency photons are used the sum frequency seen by a moving atom is velocity dependent and for oppositely propagating beams is

given by $(\nu_2-\nu_1)v/c$. Hence, one generally expects a loss of resolution due to residual Doppler broadening.[10] However, if the intermediate state is resonant, the light at ν_2 will interact most strongly with a particular velocity group. This group is composed of those atoms in the vapor which are exactly resonant, i.e., those atoms whose velocities are such that $|\nu_{ig}-(1-v/c)\nu_2| \leq \Delta\nu_i$, where ν_{ig} is the frequency separation of the intermediate to ground state transition of a stationary atom and $\Delta\nu_i$ is the natural lifetime of the intermediate state. The two-photon transition rate for this group of atoms is greatly enhanced over that for all other velocity groups. This enhencement effectively narrows the velocity distribution and in the limit of low light intensities the two-photon linewidth, $\Delta\nu_{1/2}$, is then given by

$$\Delta\nu_{1/2}=\Delta\nu_f+|(\nu_2-\nu_1)/\nu_{ig}|\Delta\nu_i, \quad (1)$$

where $\Delta\nu_f$ and $\Delta\nu_i$ are the natural widths of the final and intermediate states, respectively.[11] *The linewidth is Doppler free.* Note that if $\nu_2 \simeq \nu_1$, as in our experiment, the linewidth is insensitive to $\Delta\nu_i$ and in particular is insensitive to power broadening of the intermediate state. This method of obtaining Doppler-free spectra is completely equivalent to the technique of "laser-induced line narrowing"[12] and has been recently demonstrated as "laser-induced absorption-line narrowing."[13] We emphasize here that the technique makes it possible to simultaneously obtain high transition rates and Doppler-free spectra so that normally forbidden two-photon transitions can be studied. A detailed study of the technique as applied to two-photon transitions with unequal-frequency photons is given in Ref. 9. Salomaa and Stenholm[14] have studied theoretically a similar situation but with equal-frequency photons.

The experimental setup consisted of two single-axial-mode cw dye lasers whose unfocused outputs were propagated in opposite directions through a Pyrex cell containing sodium vapor. One laser was set to be resonant with the $3S \rightarrow 3P_{3/2}$ transition (5890 Å); the second (~5677 Å) was then swept through the two-photon resonances. One of the laser beams was chopped and two-photon transitions were monitored by observing with lock-in detection (0.3-sec time constant) the ~8190-Å fluorescence ($3D \rightarrow 3P$ transitions) that results from the decay from the $4F$ levels.

Figure 1 shows a two-photon excitation spectrum for the $3S$-$4F$ transitions taken in this manner. The observed linewidths are 34 MHz and are primarily determined by the frequency jitter

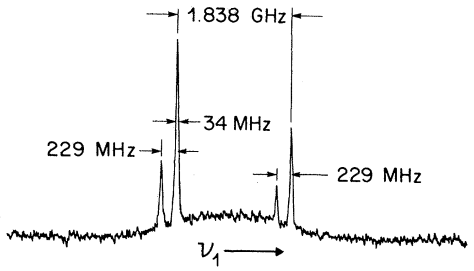

FIG. 1. The excitation spectrum for two-photon excitation of the $4F$ level with $\lambda_2=5890$ Å. The $3P_{3/2}$ level is a resonant intermediate state. Proceeding in the direction of higher frequency, the peaks correspond to the following transitions: $3S(F=2) \rightarrow 4F_{5/2}$, $3S(F=2) \rightarrow 4F_{7/2}$, $3S(F=1) \rightarrow 4F_{5/2}$, $3S(F=1) \rightarrow 4F_{7/2}$. The splitting 1.838 GHz corresponds to ν_1/ν_2 times the ground-state hyperfine splitting and 229 MHz is our measurement of the $4F$ fine-structure splitting.

of the two lasers. Much smaller and essentially negligible contributions to the linewidth are produced by foreign gas broadening,[15] unresolved structure caused by the hyperfine levels of the $3P_{3/2}$ intermediate state,[9] and power broadening. The ultimate resolution is limited by these line-broadening effects and any nonlinearity in laser frequency sweep. The frequency sweep was calibrated from the known hyperfine splitting of the $3S$ ground state, $\Delta_{3S}=1.772$ GHz. It can be easily shown[9,12] that when using two-photon spectroscopy, with a resonant intermediate state this splitting appears as $(\nu_1/\nu_2)\Delta_{3S}=1.838$ GHz in the spectrum. Averaging over 28 curves like that in Fig. 1 we have determined the $4F$ fine-structure splitting to be 229 ± 4 MHz.

The various resonances shown in the spectrum of Fig. 1 were identified in the following manner. An atom excited to the $4F_{7/2}$ level can only decay to the $J=\frac{5}{2}$ level of the $3D$ state, from which it can only decay to the $J=\frac{3}{2}$ level of the $3P$ state while emitting an 8195-Å photon. On the other hand, an atom excited to the $4F_{5/2}$ level can decay to either the $3D_{3/2}$ or the $3D_{5/2}$ level; from the $3D_{3/2}$ level the atom can decay to either the $3P_{3/2}$ or the $3P_{1/2}$ level while emitting a photon at either 8195 or 8183 Å, respectively. Thus, only the $3S \rightarrow 4F_{5/2}$ transition is accompanied by fluorescence at 8183 Å. The narrow-band interference filter used to obtain the data in Fig. 1 transmitted less at 8195 Å than at 8183 Å. When this filter was replaced with a broad-band filter, the ratio of the two lines corresponding to the $3S \rightarrow 4F_{7/2}$ and $3S \rightarrow 4F_{5/2}$ transitions increased from about 3:1 to about 10:1. This behavior showed

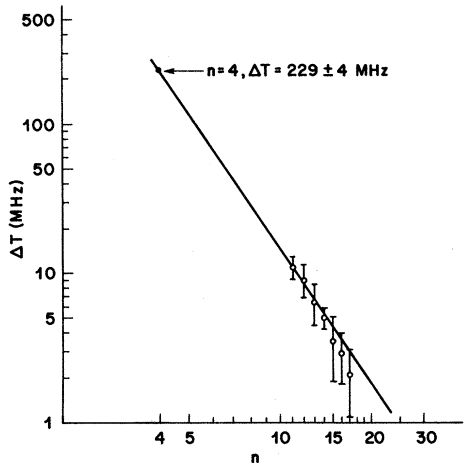

FIG. 2. Fine structure interval, ΔT, for the nF levels of sodium as a function of n. The solid point is our measurement; the open circles are taken from Ref. 6. The solid line gives the variation with n of the fine-structure interval for the nF levels in hydrogen [Eq. (2)].

that the stronger line corresponds to the $3S \rightarrow 4F_{7/2}$ transition and, consequently, that the $4F$ term splitting is normal and not inverted.

A broad background signal is also evident in Fig. 1. This signal results from resonance radiation trapping in the $3P_{3/2}$ state. This excitation of the $3P_{3/2}$ intermediate state is nondirectional and gives rise to a fully Doppler-broadened signal.

In Fig. 2 our measurement is plotted along with the measurements of Gallagher, Hill, and Edelstein.[6] All the data agree nearly exactly with the hydrogenic fine-structure interval formula

$$\Delta T_{n,l} = R\alpha^2/n^3 l(l+1). \quad (2)$$

The solid line drawn through the data is obtained with this equation. This perfect hydrogenic behavior is in sharp contrast to the D states in sodium and the F states in Rb and Cs. Those term intervals are nonhydrogenic in both magnitude and sign and do not simply scale as $1/n^3$.

It is interesting to compare the strength of the $3S \rightarrow 4F$ transition to the electric-dipole–allowed $3S \rightarrow 4D$ transition. This comparison is easily done since a fraction of excitation to the $4D$ state will decay via the $3D$ states. After taking into account the branching ratios to the $3D$ states from $4D$ and $4F$ we deduce that the $3S$-$4F$ transition is approximately 10^{-7} weaker than $3S$-$4D$.

The technique of two-photon spectroscopy with a resonant intermediate state which we have utilized in our measurement of the $4F$ fine structure should find many other applications. It will allow one to study extremely weak and nominally forbidden transitions with completely Doppler-free resolution.

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