Measurements of the lifetimes of the $7\,^2P^o_{1/2}$ and $7\,^2P^o_{3/2}$ excited states of thallium

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The lifetimes of the $7\,^2P^o_{1/2}$ and $7\,^2P^o_{3/2}$ states of thallium have been measured for the first time by observing the fluorescence decay following two-photon resonant excitation in an atomic beam. The values obtained for these states are 61.9 and 48.4 ns, respectively, with an uncertainty of 2%. These results are in good quantitative agreement with the calculations of Bardsley and Norcross, which include the effect of core polarizability.

An accurate determination of oscillator strengths for atomic transitions has been a subject of considerable interest. The neutral thallium atom has been chosen for numerous theoretical and experimental studies because of its relatively simple valence configuration. A number of calculations for thallium have been made within the framework of the one-electron approximation, both with and without the effect of core polarizability taken into account. A comparison of these theoretical values with experimental results is given by Bardsley and Norcross,[1] including the results of their own calculations. They discuss the importance of including the core-polarization effects in both the model potential and the transition-matrix elements for computing oscillator strengths and excited-state lifetimes. Although the agreement between theory and measurement is generally good for the oscillator strengths of the sharp and diffuse series of thallium, no such comparison is possible in the principal series because of the lack of experimental data. Furthermore, the measured lifetime[2] of the $9\,^2P^o_{3/2}$ state, which represents the only measurement of any $^2P^o$ excited state of thallium, differs from the calculated value by more than an order of magnitude. Reflecting on this discrepancy, Bardsley and Norcross conclude that it would be of great interest to have additional measurements of lifetimes of $^2P^o$ states or of oscillator strengths for the principal series.

The purpose of this Brief Report is to present the results of lifetime measurements for one such pair of states; the $7\,^2P^o_{1/2}$ and $7\,^2P^o_{3/2}$ states of thallium. These measurements utilize the scheme of two-photon excitation which we employed in our investigation[3] of multiphoton absorption involving an intermediate resonance in an atomic beam of thallium. This excitation scheme is advantageous because of its selective nature, which produces far fewer spectral lines than schemes using electron-beam impact excitation. Furthermore, there is no repopulation of the selected state by transitions from higher-lying levels.

Figure 1 shows the lower excited states of thallium, including those aspects of the multiphoton process pertinent to this measurement. A ground-state atom is excited to one of the $7P$ states via two-photon absorption of light from a pulsed dye-laser system. Since the conservation of energy demands that the energy of a photon equals one-half the energy of the excited state relative to the ground state, selection of either the $7\,^2P^o_{1/2}$ state or the $7\,^2P^o_{3/2}$ state is done by tuning the wavelength of the laser to this two-photon resonant condition. These wavelengths are 5853 and 5686 Å, respectively, both of which are easily obtainable from a dye laser operating with a suitable dye.[4] By monitoring the intensity of radiative transitions to lower levels as a function of time, the decay of population in the excited state can be determined. Since the wavelength of the fluorescence emitted by the $7P$-$7S$ transition is too long (>1 μm) to be easily detected by photomultiplier tubes, fluorescence originating from the $7\,^2S_{1/2}$ state to either of the $6P$ states is monitored instead. The known lifetime of the $7\,^2S_{1/2}$ state (7.4 ns) is much shorter than that of either $7P$ state. Therefore, the asymptotic behavior of the fluores-

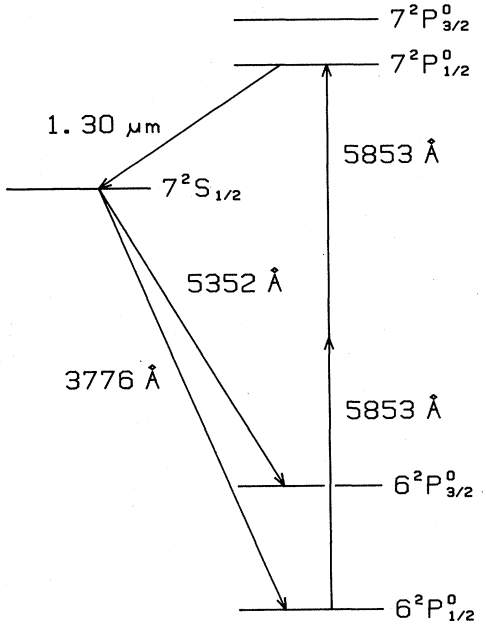

FIG. 1. Energy levels of thallium, showing excitation to the $7\,^2P^o_{1/2}$ state via two-photon absorption, followed by cascade fluorescence back down to the ground state. Changing the excitation wavelength to 5686 Å selects the $7\,^2P^o_{3/2}$ state instead.

cence signal from the $7^2S_{1/2}$ state is a simple exponential decay with a time constant equal to the lifetime of the $7P$ state, as can be shown by a simple-rate equation analysis. Similarly, neither the sampling width of the electronics nor the shape of the excitation pulse should have any effect on the decay time as long as both are shorter than that time constant. (Of course, these factors do affect just how *rapidly* the fluorescence pulse shape approaches the asymptotic single-exponential-decay behavior.)

The experimental arrangement is shown schematically in Fig. 2. The output of a frequency-stabilized cw ring dye laser is passed through a series of dye amplifiers pumped by a frequency-doubled Nd:YAG laser (YAG denotes yttrium aluminum garnet). The amplified beam is a pulse of 7 ns duration (corresponding approximately to the duration of the pulse from the Nd:YAG laser), with a peak amplitude exceeding 1 MW. For the multiphoton line-shape experiments,[5] this use of an amplified cw beam instead of a pulsed oscillator has the advantage that the spectral width of the output beam is virtually the Fourier-transform limit of the pulse duration. In the present context, however, the laser excitation only serves to populate the $7P$ states of thallium; its linewidth is not particulary important, although a narrow linewidth does tend to enhance the signal level. Not shown in the diagram are a pair of spectrum analyzers (free spectral ranges of 1.5 and 7.5 GHz, respectively), and a spectrometer used to monitor the laser frequency.

The atomic beam of thallium is illuminated by this laser beam at the center of the vacuum chamber. The fluorescence which is emitted by the atoms is sampled through the observation window and focused onto a photomultiplier tube after appropriate spectral filtering. Corning glass filters provide adequate spectral discrimination for this experiment which detected fluorescence at 3776 Å; but a spectrometer should be used if detection of the fluorescence at 5350 Å is desired. (Both wavelengths yield equivalent information.) The vacuum chamber also contains a thickness monitor to detect deposition by the atomic beam.

The fluorescence signal from the photomultiplier tube is measured by a gated integrator, and then digitized and stored in a computer. The gated integrator has a nominal gate width of 5 ns and is used in the exponential-averaging mode. As the laser repeatedly fires, the position of the gate is slowly scanned across the fluorescence pulse. The scanning of the gate is controlled externally in synchronism with the channel advance of the digitizer. For the fluorescence signal obtained in this manner, no attempt is made to normalize it to the laser intensity. The population in the excited state is a rather complicated function of laser intensity because of the nonlinear excitation process and the possible presence of saturation. Although a proper normalization is possible, the quality of the data without such normalization appears to be adequate. The shape of the leading edge of the fluorescence pulse can be affected by the average laser intensity, but no such dependence is expected in the exponential decay of the trailing edge, as was verified by changing the size of the laser beam (and hence, the intensity), at the thallium beam.

For the lifetime measurements presented in this paper, any one of the hyperfine components of the two-photon transition could be used to populate the upper state. Usually, the largest component was chosen to obtain the best signal. Figure 3 shows the time dependence of the fluorescence signal resulting from excitation of the $7^2P^o_{1/2}$ state of thallium. On this semilog plot, the trailing edge of the pulse fits quite well to a straight line as expected from an exponential decay. The slope of the line indicates a lifetime of 61.9 ns for the $7^2P^o_{1/2}$ state of thallium, whereas a similar plot for the transition to the $7^2P^o_{3/2}$ state yields a lifetime of 48.4 ns. In both cases, the error bar for the slope as derived from the statistical fit to the data indicates an uncertainty of less than a percent. Considering the repeatability of data for duplicate runs, we feel that a more conservative error estimate of 2% is appropriate for these lifetime measurements. The accuracy of the sweep range for the boxcar gate was assured to be well within this tolerance by calibrating the boxcar against a frequency counter.

Converting our measured lifetimes to absorption oscillator strengths gives values of 41.1×10^{-2} for the $7^2S_{1/2}$-$7^2P^o_{1/2}$ transition and 82.3×10^{-2} for the $7^2S_{1/2}$-$7^2P^o_{3/2}$ transition. These results compare very favorably to the theoretical values of Bardsley and Norcross which include the effect of

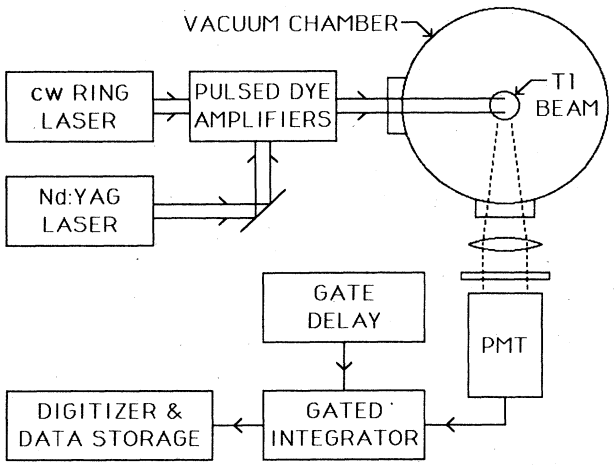

FIG. 2. Schematic of the experimental apparatus.

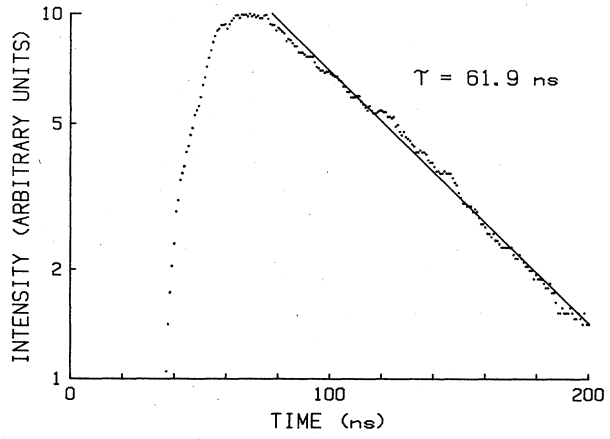

FIG. 3. Fluorescence signal at 3776 Å ($7^2S_{1/2}$-$6^2P^o_{1/2}$ transition), resulting from two-photon excitation of the $7^2P^o_{1/2}$ state of thallium. The lifetime of this state is determined by fitting the logarithm of the decaying portion of the data to a straight line.

core polarization. It is seen from their Table II that the calculated oscillator strengths for both transitions are higher than our experimental values by about 10% when core polarization is neglected, but after inclusion of this effect the agreement improves to 1% and 3%, respectively. The latter deviations are comparable to the uncertainty of our measurements.

With appropriate changes in excitation frequency, our method could be used to investigate the lifetimes of other $^2P^o$ states as well. For example, a two-photon resonance to the $9^2P^o_{3/2}$ state requires light at 4488 Å, which may be easily obtained with conventional pulsed dye lasers pumped by a frequency-tripled Nd:YAG output. The high selectivity of this method allows population of just one initial excited state, thereby reducing drastically the number of subsequent cascade transitions. Not only does this mean a larger signal for each transition, but it also reduces the possibility of misidentification of fluorescent components, which may occur when a myriad of excited states are populated indiscriminately.[1] Our measurements demonstrate that two-photon excitation offers an attractive alternative to other methods for determining the lifetimes of such states.

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[1]J. N. Bardsley and D. W. Norcross, J. Quant. Spectrosc. Radiat. Transfer **23**, 575 (1980).

[2]L. L. Shimon and N. M. Erdevdi, Opt. Spektrosk. **42**, 241 (1977) [Opt. Spectrosc. **42**, 137 (1977)].

[3]C. C. Wang, J. V. James, and J. Xia, Phys. Rev. Lett. **51**, 184 (1983).

[4]The operating wavelength of 5686 Å lies between the gain peaks of Rhodamine 590 and Rhodamine 560 laser dyes for the cw laser. Contrary to information given us which suggested that it would not work well with cw pumping, we found that Rhodamine 575 works very well at this wavelength.

[5]J. V. James and C. C. Wang (unpublished).