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Determination of radiative lifetimes of excited states in neutral gold using time-resolved vacuum-ultraviolet laser spectroscopy

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Natural radiative lifetimes of the states in the highly perturbed $5d^{10}np^2P$ sequence in neutral gold, Au I, for $n=6-9$, as well as of four of the perturbing $5d^96s6p^2P$ states, have been measured. This was done by direct excitation from the ground state with short-pulse vacuum-ultraviolet laser light and time-resolved detection of the laser-induced fluorescence. We found the lifetimes to be $\tau(6p^2P_{1/2})=6.2(2)$ ns, $\tau(6p^2P_{3/2})=4.7(2)$ ns, $\tau(7p^2P_{1/2})=6.4(7)$ ns, $\tau(7p^2P_{3/2})=5.3(7)$ ns, $\tau(8p^2P_{1/2})=63(3)$ ns, $\tau(8p^2P_{3/2})=24(2)$ ns, $\tau(9p^2P_{1/2})=28(2)$ ns, and $\tau(9p^2P_{3/2})=75(4)$ ns. For the perturbing states (two states of each term have been observed) we found $\tau(^2P_{1/2}, 60\,983.05\text{ cm}^{-1})=17.5(10)$ ns, $\tau(^2P_{1/2}, 62\,540.65\text{ cm}^{-1})=6.7(7)$ ns, $\tau(^2P_{3/2}, 58\,826.30\text{ cm}^{-1})=2.1(15)$ ns, and $\tau(^2P_{3/2}, 63\,005.62\text{ cm}^{-1})=2.7(15)$ ns. Furthermore, we have investigated the hyperfine structure of the $6p^2P_{3/2}$ state.

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I. INTRODUCTION

Gold is among the few heavy elements that have a simple electronic structure. The ground state is $(5d)^{10}6s^2S_{1/2}$: a single $6s$ electron outside a closed d shell. However, since the $5d$ shell can easily break up, doubly excited states are present below the ionization threshold, and these states, formed from the $(5d)^96s6p$ and $(5d)^8(6s)^26p$ configurations, strongly perturb the $(5d)^{10}np$ Rydberg series. Three open shells make a complete calculation a difficult task and the need for a relativistic treatment for this heavy atom is a further complication. We have measured the natural radiative lifetimes in the 2P sequence for $n=6-9$ and some of these were found to be very short. The lifetimes of four of the perturbing states in the $(5d)^96s6p$ configurations have also been measured. The relevant energy levels [1,2] in the neutral gold atom are shown in Fig. 1. Previously only lifetimes of the $(5d)^{10}6p^2P$ states have been measured. These measurements were made using pulsed laser excitation in a rare-gas discharge [3], level-crossing spectroscopy [4], by electronic-beam excitation [5], and by beam-foil excitation [6].

Only recently it has become possible to use nonlinear effects in crystals and gases to produce tunable radiation with relatively high power in the vacuum-ultraviolet (vuv) region. The vuv laser system at the Lund High-Power Laser Facility is capable of producing short (7–8 ns), narrow-band pulses at wavelengths down to 120 nm

and is very useful for direct excitation of high-lying levels in atoms or ions, as required in the present experiment.

II. EXPERIMENTAL SETUP

The experimental setup used in the present experiment is shown in Fig. 2. Since it has been described in detail elsewhere [7,8], we will here give only a brief review.

The tunable vuv radiation required to excite the states of interest was produced from two uv beams by resonant four-wave mixing in krypton. In this way we could effectively produce light in the vuv spectral region, required for the present study. The frequency conversion cell windows were made of lithium fluoride as well as the dispersive prism in the monochromator used to separate

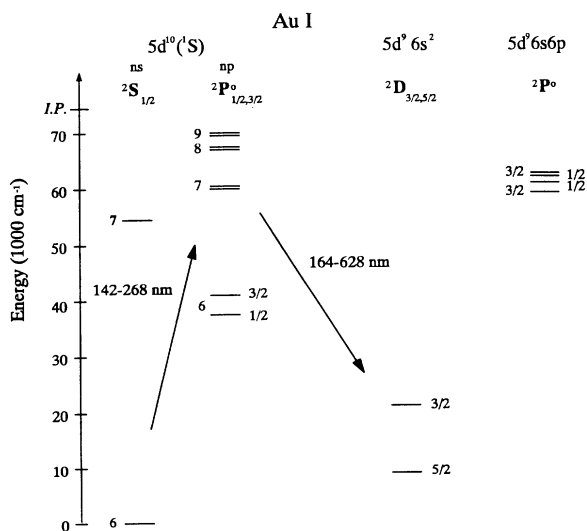


FIG. 1. Partial energy-level diagram for the gold atom with transition wavelength ranges indicated.

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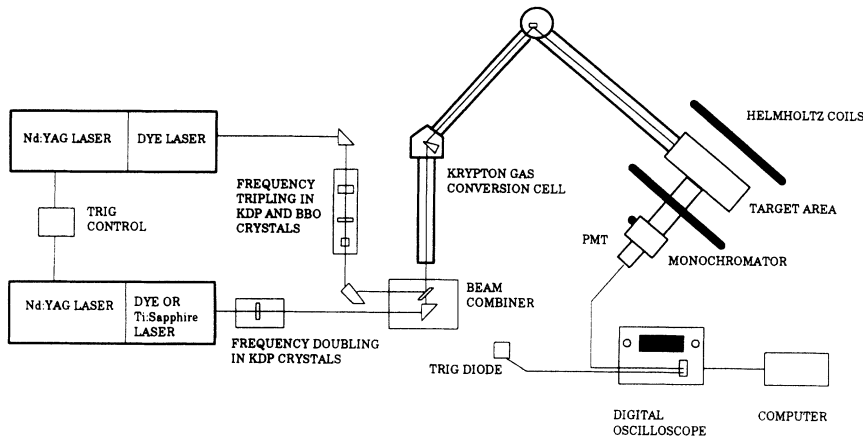


FIG. 2. Experimental setup for time-resolved laser spectroscopy experiments on gold atoms.

the vuv light from the two uv beams. The final vuv pulses carried an energy of a few μJ .

The uv beams were produced by frequency doubling or tripling the output from dye or Ti:sapphire lasers. Two pulsed, frequency-doubled Nd:YAG (where YAG denotes yttrium aluminum garnet) lasers (maximum output energy 750 mJ at 532 nm) were used as pump lasers. One was pumping a dye laser operating on a DCM dye at the wavelength 637.662 nm, the other one was pumping either a Ti:sapphire laser or another dye laser, operating on different dyes to cover the desired wavelength region. The pump lasers were externally triggered to ensure a good temporal overlap of the output pulses.

The output from the DCM dye laser was frequency doubled in a potassium dihydrogen phosphate (KDP) crystal and mixed with the fundamental radiation in a β -barium borate (BBO) crystal to produce the third harmonic at 212.554 nm, having an energy of approximately 5 mJ. The output from the other laser—a dye laser or a Ti:sapphire laser—was frequency doubled in a KDP crystal.

The vuv light was conducted through vacuum tubes to the target area to cross a gold atomic beam at right angles. The atomic beam was produced by heating pure gold in a ceramic oven to a temperature of about 1100 °C.

As some of the states in the 2P sequence have lifetimes comparable to the duration of the laser pulse, we have also used another laser system that produces considerably shorter pulses. Thus the $6p\ ^2P$ states were excited by 70-ps pulses with near Fourier-limited bandwidth. These short pulses were obtained by pumping a dye laser with a distributed feedback oscillator [9], which was pumped by a picosecond mode-locked Nd:YAG laser. A detailed description of this laser system will be given separately [10].

The output from the picosecond dye laser was frequency doubled in a KDP crystal. To generate radiation at the resonance lines at 267.65 and 242.73 nm, respectively, the radiation was subsequently mixed with the fundamental of either the pump laser (1064 nm) or the dye laser for excitation of the $6p\ ^2P_{1/2}$ and $^2P_{3/2}$ states, respectively. The resulting uv light was carrying an energy of approximately 100 μJ . In order to measure short lifetimes as accurately as possible one would of course want to use the picosecond dye laser to generate vuv light as well. We

are not yet capable of doing this, but work is being done to accomplish it [10]. So far we have only been able to study the $6p$ states with the picosecond dye laser.

On the detection side—at right angles to the exciting light as well as to the atomic beam—we have used various filters or a monochromator together with a solar-blind Hamamatsu R1220 photomultiplier tube (PMT). This type of PMT is immune to the strong emission from the hot atomic-beam oven. In the ps experiment we used a very fast microchannel plate PMT (Hamamatsu R1564U), with a rise time of 0.2 ns. The fluorescence signals were recorded using a transient digitizer (Tektronix DSA 602 or TDS 620) and were then transferred to a personal computer for storage and subsequent analysis.

III. MEASUREMENTS

Figures 3(a) and 3(b) show examples of the recorded fluorescence from two different states, the $6p\ ^2P_{3/2}$ and the $9p\ ^2P_{1/2}$ states. The lifetimes of the longer-lived states were obtained by fitting an exponential to the recorded signal for times late enough for the excitation pulse to have completely died off. This method was not appropriate for the short-lived states ($\tau < 15$ ns), since the duration of the laser pulse was 7–8 ns. For these states the laser pulse was recorded with the same detector system as used for registration of the fluorescence. The convolution of the laser pulse with an exponential was fitted to the experimental fluorescence decay curves.

For each state we have varied several experimental parameters. To ensure the absence of multiple scattering that could otherwise influence the lifetime, we have changed the atomic density over one order of magnitude. For the short-lived states, where pulse deconvolution was used, we varied the intensity of the laser light to establish that saturation of the transitions did not present a problem. Both of these possible sources of error are of course most threatening for the lowest states, as these transitions are the strongest. The atomic density was low enough during all measurements for collisions to be completely absent. None of these variations was observed to cause any change in the lifetimes.

When evaluating lifetimes one should also be aware of modulations (quantum beats) of the signal that can

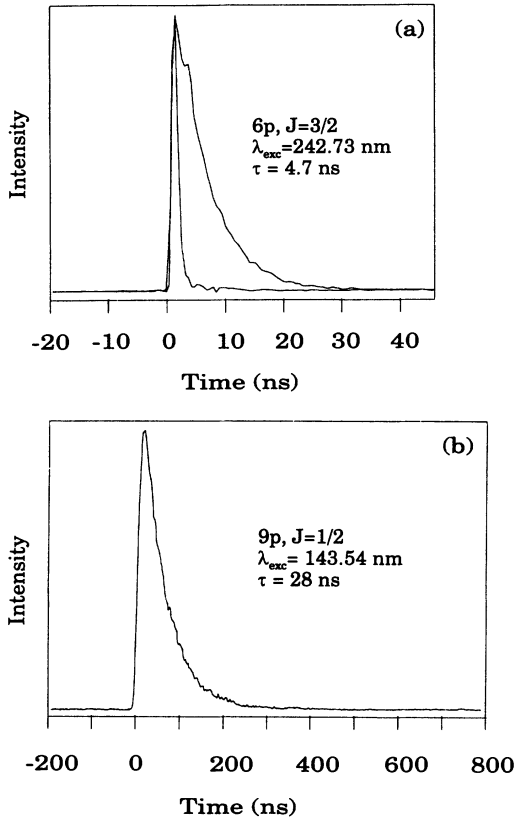


FIG. 3. Recorded fluorescence curves from (a) the $6p\ ^2P_{3/2}$ and (b) the $9p\ ^2P_{1/2}$ states of neutral gold. A recording of the exciting laser pulse is included in (a).

severely impair a precise measurement. Quantum beats are not at all present for the $J=\frac{1}{2}$ states due to the geometry of the experiment and the linear polarization of the laser light. For the short-lived states with $J=\frac{3}{2}$, quantum beats originating in the Zeeman effect can be neglected, since the magnetic field of the earth will at most induce a modulation of a few MHz, which will have no significant effect during a few nanoseconds. For the longer-lived states with $J=\frac{3}{2}$ we applied a magnetic field from Helmholtz coils to cancel out the earth magnetic field.

Quantum beats originating from the hyperfine structure could be avoided for the $6p\ ^2P_{3/2}$ state by detecting

light with polarization at an angle of 54.7° relative to the polarization of the exciting light, in zero magnetic field. In order to resolve the beats for the hyperfine structure light with polarization perpendicular to that of the exciting laser radiation was detected. As we do not have a polarizer for light in the vuv region we could not apply the same technique to hyperfine quantum beats for the states with $n > 6$. However, we could vary the polarization of the exciting light, and we found that it did not influence the evaluated lifetimes.

IV. RESULTS AND DISCUSSION

In Tables I and II all the measured natural radiative lifetimes are listed. Error bars are given in units of one in the last digit: $6.2(2)$ means 6.2 ± 0.2 . The uncertainty in the lifetime values is mostly given by the statistical variation, and for the short-lived states there is also a systematic error of $0.05\text{--}0.1$ ns originating in the deconvolution of the system temporal response function. As can be seen in Table I, the p sequence is distorted, and the lifetimes do not in any way follow an $(n^*)^3$ dependence, typical of a Rydberg series. This is expected since there is probably a strong interaction with the $(5d)^96s6p$ configuration and large relativistic effects would be present in the heavy gold atom.

Our values for the $6p\ ^2P$ states are in excellent agreement with the ones obtained by Hannaford, Larkins, and Lowe [3] in an experiment similar to ours; however, gold atoms were produced by sputtering in a rare-gas discharge. Also the results obtained in the level-crossing experiment [4] for the $6p\ ^2P_{3/2}$ state agree very well with ours, whereas the method of electron-beam excitation [5] seems to give too large values for the lifetimes. The beam-foil data [6] agree with ours within the rather large error bars of the earlier study. Clearly, the laser methods employing selective excitation are expected to yield more reliable results than the nonselective techniques.

The $7p\ ^2P$ states are particularly short-lived. The precision is limited by a large statistical variation. Since the 2P states of the $(5d)^96s6p$ configuration are very close in energy to $7p$, there is probably a large mixing of states involved.

For the higher-lying levels— $8p$, $9p$, and $10p$ —we observed a tendency of preferred decay to the metastable 2D state, a decay with $\Delta J = +1$, rather than back to the

TABLE I. Measured lifetimes in the $(5d)^{10}np$ sequence of neutral gold.

State $np\ ^2P_J$	Excitation wavelength (nm)	Lifetime (ns)	
		This study	Lit. data
$6p\ ^2P_{1/2}$	267.65	6.2(2)	6.0(1) [3], 7.4(7) [5], 7.4(15) [6]
$^2P_{3/2}$	242.73	4.7(2)	4.6(2) [3], 4.6(3) [4], 5.3(10) [5], 4.3(5) [6]
$7p\ ^2P_{1/2}$	166.63	6.4(7)	
$^2P_{3/2}$	164.72	5.3(7)	
$8p\ ^2P_{1/2}$	149.37	63(3)	
$^2P_{3/2}$	148.14	24(2)	
$9p\ ^2P_{1/2}$	143.54	28(2)	
$^2P_{3/2}$	142.88	75(4)	

TABLE II. Measured lifetimes of four of the 2P states of the $(5d)^96s6p$ configuration of neutral gold.

State $6s6p\ {}^2P_J$	Excitation wavelength (nm)	Lifetime (ns)
$6s6p\ {}^2P_{3/2}$	169.99	2.1(15)
${}^2P_{1/2}$	163.98	17.5(10)
${}^2P_{1/2}$	159.87	6.7(7)
${}^2P_{3/2}$	158.72	2.7(15)

ground state as for the lower states.

For the $10p\ {}^2P_{1/2}$ state, there has been some ambiguity in the identification. Brown and Ginter [2] have observed two levels lying very close in energy, one of which is the $10p\ {}^2P_{1/2}$ state and the other one was identified as an interloper level. We observed only one of these states, at 140.69 nm or $71\,078.51\text{ cm}^{-1}$ above the ground state, which is what Brown and Ginter have called the interloper level. But since we observed fluorescence due to decay to the metastable state, at $49\,618.93\text{ cm}^{-1}$, and this same line, at $49\,618.8945\text{ cm}^{-1}$, has been identified as a gold line in a Fourier transform spectrum of a hollow-cathode discharge [11], we believe that this is the $10p\ {}^2P_{1/2}$ state. We tried to measure the lifetimes of the $10p\ {}^2P$ states as well, but the transitions were very weak. A rough estimate would be 10(5) ns for the $J=\frac{1}{2}$ state and 90(30) ns for the $J=\frac{3}{2}$ state.

The lifetimes of four of the 2P states of the $(5d)^96s6p$ configuration have been measured as well and are given in Table II. Brown and Ginter [2] have reported two levels of each 2P_J term, and since there is a large uncertainty in the labeling of these levels, they have only been specified by their respective energies. The values given for the very short-lived $J=\frac{3}{2}$ states are only estimates to within 50%, as the relative accuracy is reduced when the lifetime is much shorter than the exciting laser pulse.

By fitting a theoretical intensity curve, including quantum beats, to the experimental curve, the magnetic dipole interaction constant A and the electric quadrupole interaction constant B for the hyperfine structure of the $6p\ {}^2P_{3/2}$ state were evaluated to be $A=13.9(8)$ MHz, $B=331(6)$ MHz. They are found to be in excellent agreement with the results, $A=14.0(5)$ MHz and $B=327.6(1.6)$ MHz, obtained by Einfeld, Ney, and Wilken [4] using the level-crossing technique.

Finally, Table III presents a comparison between theoretical and experimental values for the oscillator strengths of the $6p\ {}^2P_{1/2}-6s\ {}^2S_{1/2}$ and $6p\ {}^2P_{3/2}-6s\ {}^2S_{1/2}$ transitions. To convert our values for the lifetimes to absorption oscillator strengths we have used the results ob-

TABLE III. Comparison of experimental and theoretical absorption oscillator strengths for the $6p\ {}^2P_{1/2,3/2}-6s\ {}^2S_{1/2}$ transitions.

Oscillator strength Transition		Method
1/2-1/2	3/2-1/2	
0.170(7) ^a	0.344(16) ^a	Nonrelativistic HF
0.176(3) ^b	0.351(15) ^b	
0.631 ^c	1.262 ^c	
0.390 ^c	0.791 ^c	
0.296 ^c	0.623 ^c	Relativistic HF
0.158 ^d	0.36 ^d	Relativistic MCHF
		Relativistic HF including core polarization

^aThis experiment, using branching ratios measured by Hannaford, Larkins, and Lowe [3].

^bReference [3].

^cReference [12].

^dReference [13].

tained by Hannaford, Larkins, and Lowe [3] for the branching ratios of these two transitions, and the uncertainties given are obtained from $\Delta f/f = \Delta R/R + \Delta\tau/\tau$, with ΔR taken from [3]. The results obtained by Migdalek and Baylis [13] in a relativistic Hartree-Fock (HF) calculation including effects of core polarization seem to agree quite well with the experimental results. The results of Desclaux and Kim [12] show a somewhat larger discrepancy with the experimental values, but seem to show a correct tendency going from a nonrelativistic HF to a relativistic single-configuration HF calculation to a relativistic multiconfiguration Hartree-Fock (MCHF) calculation (two configurations in the ground state, two configurations in the excited state), and suggest inclusion of a large number of configurations. On the ground state $6s\ {}^2S_{1/2}$ a many-body perturbation theory approach has been used with great success [14].

Gold is one of the few heavy atoms with a relatively simple electronic structure, in which most of the bound states form Rydberg series. The combination of this with large relativistic effects and strong electron correlation can make it an excellent test case for a large-scale relativistic calculation, that will be of fundamental methodical interest. We hope that the data presented in this work, showing the perturbation of the $(5d)^{10}np\ {}^2P$ series in atomic gold through extremely short lifetimes, will spur such calculations.

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