Determination of Radiative Lifetimes In the 3d(10)np(2)p Sequence of Neutral Copper By Time-resolved Vuv Laser-spectroscopy

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Determination of radiative lifetimes in the $3d^{10}np\ ^2P$ sequence of neutral copper by time-resolved vuv laser spectroscopy

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Lifetimes in the $3d^{10}np\ ^2P$ sequence in neutral copper were measured by time-resolved laser spectroscopy. Excitation from the ground state was performed with pulsed laser radiation in the vuv spectral region, generated by resonant sum-difference four-wave mixing in krypton gas. The lifetimes were evaluated from recorded optical transients. For the $np\ ^2P_J$ states we find the following: $\tau(n=6,J=3/2)=5.2(8)$ ns, $\tau(6,1/2)=25.1(10)$ ns, $\tau(7,3/2)=15.0(12)$ ns, $\tau(7,1/2)=4.0(8)$ ns, $\tau(8,3/2)=31(2)$ ns, $\tau(8,1/2)=15.8(12)$ ns, $\tau(9,3/2)=123(6)$ ns, and $\tau(9,1/2)=51(6)$ ns. The data are compared with a recent multiconfiguration Hartree-Fock calculation.

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I. INTRODUCTION

Investigating the P sequence of neutral copper is a challenging task for both experimentalists and theoerticians. Strong configuration interaction with the doubly excited $3d^9 4s4p$ states gives rise to irregular fine structures. Anomalously short lifetimes have been predicted as well as irregular hyperfine structures [1]. This series has been said to be "probably the most distorted series known" [2]. Lifetime measurements using selective excitation have previously been performed for the $3d^{10}4p$ and $5p$ states [3–5]. For the $6p$ and $7p$ states electron-beam excitation measurements exist [6–8]. The aim of this work was to obtain accurate lifetime data of these states using selective excitation.

Experimental difficulties in studies of the P states are due to the relatively short lifetimes in the sequence and the fact that all levels but one are situated more than 48 000 cm^{-1} above the ground state, as shown in Fig. 1. Hence, energetic photons for excitation are required. One way of avoiding this difficulty is to populate the metastable $3d^9 4s^2$ state in a hollow cathode discharge [3,9,10]. However, the metastable state is only about 13 000 cm^{-1} above the ground state and uv excitation is still needed to reach the higher-lying P states. There are also several disadvantages with this technique. The population in the metastable state is relatively low, which reduces the signal. Systematic errors due to collisions in the discharge region as well as background noise from the discharge may be introduced. In view of these facts, we chose to perform the excitation from the ground state employing vuv laser radiation. Efficient vuv sources for pulsed laser radiation have recently become available through resonant sum-difference four-wave mixing in rare gases [11].

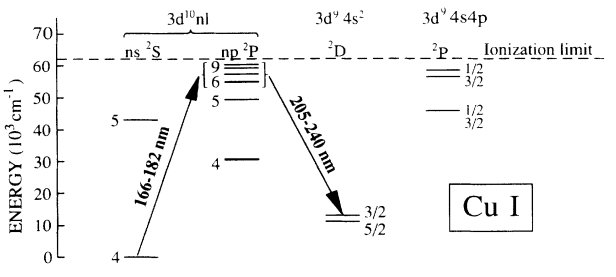

FIG. 1. Partial energy-level diagram for the copper atom with relevant transitions indicated.

The most favorable four-wave-mixing scheme for producing vuv radiation is sum-difference mixing $\omega_{vuv}=2\omega_R-\omega_T$, since there are no restrictions on the sign of the wave-vector mismatch. By tuning the sum frequency ω_R to a two-photon resonance, a large enhancement in conversion efficiency can be achieved. To produce vuv radiation with a wavelength longer than the lithium fluoride (LiF) transmission cutoff (110 nm), the $4p$-$5p[1/2,0]$ transition (in the jk notation) in krypton is an appropriate choice for the resonant two-photon level for the sum frequency [Fig. 2(a)]. By mixing the sum frequency with the output from a dye laser (fundamental or frequency doubled) or a Ti:sapphire laser (fundamental, frequency doubled, or frequency tripled), the whole range of 120–200 nm can be covered, as shown in Fig. 2(b).

II. EXPERIMENTAL SETUP

The experimental setup used in the present experiments is shown in Fig. 3. To obtain the required vuv radiation, nonlinear frequency mixing in several steps was performed. The frequency-doubled outputs of two Continuum Model No. NY82-10 injection-seeded and Q-switched Nd:YAG (where YAG denotes yttrium aluminum garnet) lasers were used to pump two tunable lasers. The two pump lasers were externally triggered by a Stanford Research System Model No. 535 delay unit to obtain good temporal overlap of the two beams.

One of the tunable lasers was a Continuum Model No. ND60 nanosecond dye laser operating on DCM dye and was tuned to the wavelength 637.66 nm. The dye-laser radiation was, first, frequency-doubled in a KDP (potassi-

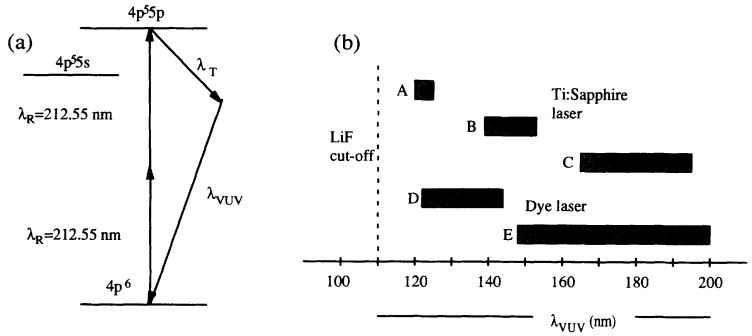

FIG. 2. (a) Partial energy-level scheme for krypton, showing resonantly enhanced sum-difference mixing to produce vuv radiation. (b) Tuning range of the resonant frequency mixing $\omega_{vuv}=2\omega_R-\omega_T$, with $\lambda_R=212.55$ nm and with ω_T as the output from A, fundamental Ti:sapphire laser; B, frequency-doubled Ti:sapphire laser; C, frequency-tripled Ti:sapphire laser; D, fundamental dye laser; and E, frequency-doubled dye laser.

um dihydrogen phosphate) crystal and then mixed with the fundamental frequency in a BBO (β-barium borate) crystal to produce effectively the third harmonic of the dye laser at 212.55 nm. (To make the mixing possible, a mechanically compressed crystalline quartz plate is used to rotate the polarizations of the fundamental and the doubled dye-laser beams to obtain parallel polarization components before the BBO crystal.) This radiation is two-photon resonant with the $4p$-$5p$ [1/2,0] transition in krypton. The frequency mixing gave a pulse energy at 212.55 nm of about 7 mJ.

To produce wavelengths between 166 and 183 nm, the uv output was mixed with near-uv radiation. This radiation was obtained from another frequency-doubled ND60 dye laser or a frequency-tripled Continuum Model No. TS60 Ti:sapphire laser, pumped by the second Nd:YAG laser.

The four-wave-mixing unit was specially designed for our laser system by GWU-Lasertechnik and consists of a beam combiner, a converting cell, and a LiF monochromator. The two laser beams are combined and focused by a 30-cm-focal-length uv achromat for good spatial overlap inside the 55-cm-long conversion cell. The conversion cell is separated from the vacuum system by a LiF lens and the vuv radiation is isolated from the two fundamental beams in a high-efficiency LiF monochromator. The vuv radiation produced had a pulse energy of several μJ. The pulse duration was less than 10 ns. For the measurements of the $6p\ ^2P_{1/2,3/2}$ state lifetimes, requiring excitation at 182 nm, shorter and more energetic laser pulses could be produced using stimulated Raman shifting. The dye laser operating on Lambdachrome 6500 was tuned to 642 nm. The radiation was frequency-tripled and Raman-shifted in a cell filled with 10 bar of hydrogen. The second anti-Stokes component can then be made resonant with the $6p\ ^2P_{1/2,3/2}$ states.

The vuv beam was sent through vacuum tubes into the experimental chamber in order to suppress air absorption in the Schumann-Runge molecular oxygen bands. Free copper atoms were produced as a beam from an oven in the vacuum system. The pressure in the vacuum chamber was about 1 mPa. Fluorescence light was detected (perpendicularly to the vuv beam) in the decay in the $3d^94s^2\ ^2D$ states with a Hamamatsu Model No. R1220 photomultiplier tube in a magnetic shield case preceded by an interference filter or a 0.2-m monochromator. The signals were acquired with a Tektronix Model No. DSA 602 digital oscilloscope and were transferred to an IBM-compatible computer for evaluation. Time-resolved recordings of the fluorescence intensity from the $6p$ and $8p\ ^2P_{3/2}$ states are shown in Fig. 4.

III. MEASUREMENTS AND RESULTS

Several series of measurements were performed for each state. To make sure that the experimental result

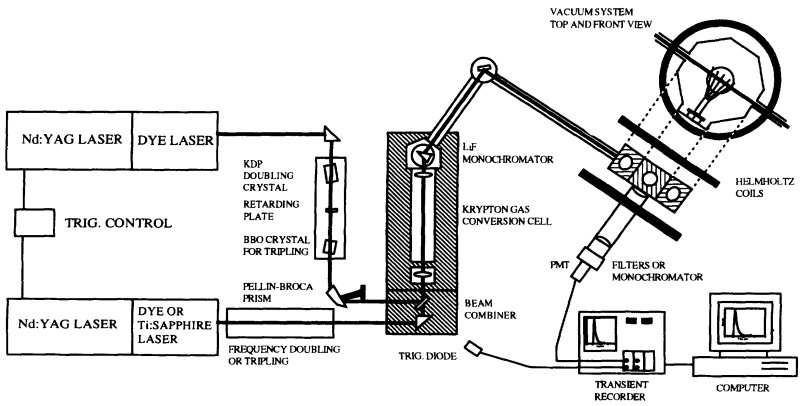

FIG. 3. Experimental setup for time-resolved vuv laser spectroscopy. PMT denotes a photomultiplier tube.

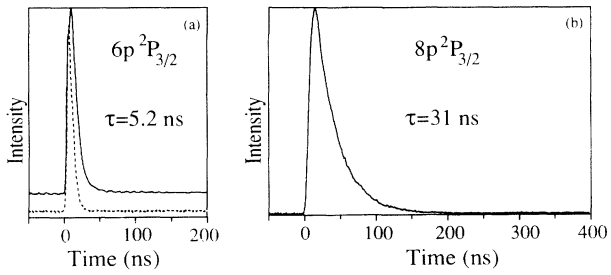

FIG. 4. Recording of the time-resolved fluorescence from the (a) $6p\ ^2P_{3/2}$ and (b) $8p\ ^2P_{3/2}$ states of neutral copper. The excitation laser pulse is shown as a dashed line in (a).

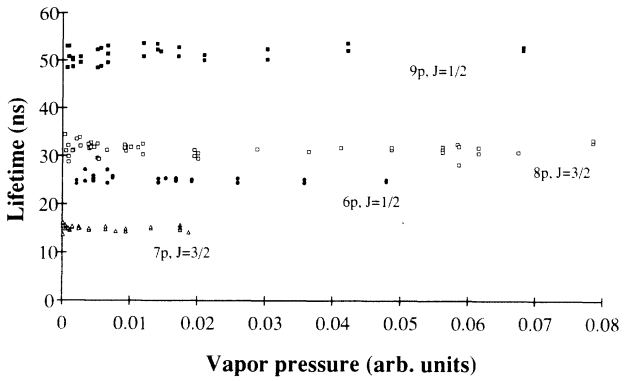

FIG. 5. Plots of evaluated experimental lifetime values for the $np\ ^2P_J$ states of Cu I as a function of copper atomic beam density. The diagram shows that the lifetime values are unaffected by multiple scattering and atom-atom collisions.

was not influenced by light multiple scattering or atom-atom collisions, the atomic density as well as the background pressure were varied for each series of measurements. This is particularly important when using vuv excitation. Since laser pulse energies may be low, it is tempting to run too strong an atomic beam to recover the signal. The efficiency and usefulness of our new vuv source is well illustrated in Fig. 5, showing that lifetime values can be obtained under quite unperturbed conditions. A pair of Helmholtz coils produced a magnetic field of about 5 mT to wash out Zeeman quantum beats for the long-lived states, for which otherwise deviations from a pure exponential decay curve could occur due to slow precision in the earth's magnetic field. For the short-lived states, however, the latter field was canceled to avoid appreciable precision during the brief observation time pertaining to that case. It could be noted that a very low contrast in the quantum beats is expected for the J-value sequence in the excitation-detection scheme used. Hyperfine-structure quantum beats, possible only for the $^2P_{3/2}$ states, did not influence the measurements because of low modulation contrast and unpolarized detection.

The decay constants for the long-lived states were obtained by computer fitting of an exponential for times late enough to be outside the duration of the laser pulse. For the short-lived states the decay constants were evaluated by fitting the experimental decay curve to a convolution of an exponential decay and the recorded laser pulse. The pulse length under these measurements was approximately 7 ns. For the short-lived states, where the temporal structure of the vuv pulse was included in the fit, the laser power was also varied to make sure that the transition was not saturated. The data obtained for the ($n=6-9$) $n\ ^2P$ states are given in Table I, together with literature experimental data for $n=4-7$.

The transitions from the higher-lying states in the ^2P sequence to the $3d^9 4s^2\ ^2D$ states following electric

TABLE I. Experimental and theoretical values of the radiative lifetimes of the ($n=4-9$, $J=1/2,3/2$) states in the $3d^{10}np\ ^2P$ sequence of neutral copper.

State	λ_{exc} (nm)	Radiative lifetime (ns) Theory[a]	Experiment
$3d^{10}4p\ ^2P_{1/2}$	327.5	6.87	7.27(6)[b]
$3d^{10}4p\ ^2P_{3/2}$	324.8	6.68	7.17(6)[b]
$3d^{10}5p\ ^2P_{1/2}$	202.5	19.5	27.1[c]
$3d^{10}5p\ ^2P_{3/2}$	202.5	16.5	25.5(10),[d] 23(2),[e] 27.9[c]
$3d^{10}6p\ ^2P_{1/2}$	181.7	19.5	25.1(10),[f] 23[g]
$3d^{10}6p\ ^2P_{3/2}$	182.5	4.92	5.2(8),[f] 6.2[g]
$3d^{10}7p\ ^2P_{1/2}$	174.2	4.37	4.0(8),[f] 5.8[g]
$3d^{10}7p\ ^2P_{3/2}$	172.6	5.76	15.0(12),[f] 17[g]
$3d^{10}8p\ ^2P_{1/2}$	168.6	5.19	15.8(12)[f]
$3d^{10}8p\ ^2P_{3/2}$	168.8	10.6	31(2)[f]
$3d^{10}9p\ ^2P_{1/2}$	166.5	8.51	51(3)[f]
$3d^{10}9p\ ^2P_{3/2}$	166.5	22.7	123(6)[f]

[a]Reference [1].
[b]Reference [3].
[c]Reference [7].
[d]Reference [5].
[e]Reference [4].
[f]This work.
[g]Reference [6].

discharge population from the ground state have been suggested as a possible uv laser scheme [1]. The short lifetime of the $7p\ ^2P_{1/2}$ state implies that this state could be a suitable upper laser level since population of the lower state from other transitions does not present a problem in a discharge population scheme. Another requirement of a gas discharge laser is that the pump transition from the ground state should be stronger than that between the two laser levels. By using a vuv monochromator connected to the vacuum system, we could investigate the relative oscillator strengths. Unfortunately, the transition to the $3d^9 4s^2\ ^2D$ state was shown to be one order of magnitude stronger than to the ground state, which would make the inverted population difficult to attain.

The results of this radiative lifetime study are compared with a theoretical calculation by Carlsson [1], using the multiconfiguration Hartree-Fock approach. For the lower-lying state, the agreement is rather good, but for higher lying states, the agreement is poor. This indicates an overestimated configuration interaction with the $3d^9 4s 4p$ states in the calculations.

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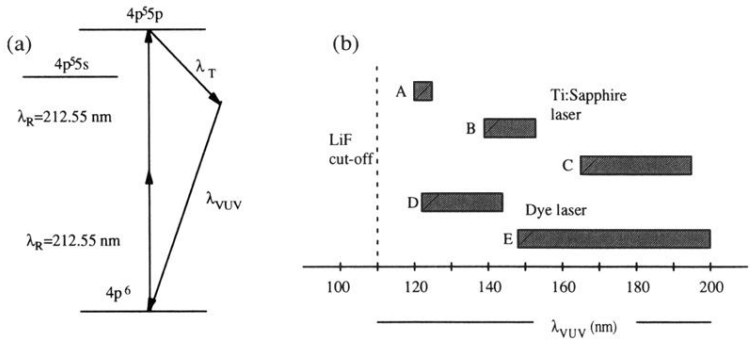

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