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Determination of radiative lifetimes of neutral bismuth by time-resolved uv-vuv laser spectroscopy

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Time-resolved laser spectroscopy was used to measure natural radiative lifetimes of ten excited states of neutral bismuth. Four levels of the $6p^2ns\,^4P_{1/2}$ sequence ($n=7,8,9,10$) and the $6p^27s\,^4P_{3/2,5/2}$ and $6p^2nd\,^2D_{3/2;5/2}$ ($n=6,7$) levels were investigated. The results are compared with previous data when possible. Revised absolute transition probabilities for 26 lines are given. Several levels required vacuum-ultraviolet (vuv) excitation, which was achieved by stimulated anti-Stokes Raman shifting of frequency-tripled dye-laser radiation in high-pressure H_2 gas.

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I. INTRODUCTION

Bismuth is the heaviest stable atom and has a rather simple term structure. Thus, it is favorable for the testing of relativistic calculations. Recently the first *ab initio* fully relativistic calculation on bismuth was performed by Bieron and Migdalek [1]. The radiative lifetimes of the levels belonging to the $6p^27s$ configuration were calculated by the multiconfiguration Dirac-Fock method. Semiempirical calculations have been performed earlier by Holmgren [2] and Kunisz and Migdalek [3]. As it is a heavy atom with a large nuclear spin, bismuth is used for testing the standard model of electroweak interactions. Recently, parity nonconservation has been measured in bismuth with high accuracy by MacPherson *et al.* [4].

The first radiative lifetime measurement for the resonance state $6p^27s\,^4P_{1/2}$ of bismuth was performed by Cunnigham and Link using the phase-shift method [5]. Further states were studied by Svanberg using the Hanle method [6]. In both experiments optical excitation by resonance lamps was used. There are certain difficulties in using the Hanle method in the case of bismuth because of the influence of hyperfine structure. Experiments with nonselective excitation have also been performed. Thus, beam-foil excitation was used by Andersen, Madsen, and Sorensen [7], and electron-beam excitation by Osherovich and Tezikov [8]. The number of states with reported lifetime values in this way increased to 18. The lifetimes of the short-lived states $6p^27s\,^2P_{3/2}$, $^4P_{5/2}$ were also deduced by Poulsen and Hall from an analysis of the observed Doppler-free line profile using narrow-band laser excitation to a specified hyperfine level [9]. The first direct measurement of lifetimes using laser excitation was performed by Carlsson for the resonance state $6p^27s\,^4P_{1/2}$ [10]. The lifetime, which was measured with the single-photon counting delayed-coincidence method, has a very high accuracy and can be used as a reference value. A poor agreement with data reported in Refs. [7] and [8] is observed, while agreement with data from Ref. [5] is good. Nonselective excitation leading to cascading might have influenced the data in Refs. [7] and [8].

Transition probabilities for 29 uv lines of Bi have been measured in the emission from an arc by Corliss and Bozman in their classical work [11], but these results are known to be rather inaccurate. Transition probabilities were obtained by Guern *et al.* [12] from measured branching ratios and lifetimes taken from literature [6–8]. The arithmetic mean value of all available literature data was used, and the weight of data from Refs. [7] and [8] is large. Therefore, if the lifetimes obtained by nonselective excitation [7,8] are systematically deviating, inaccurate transition probabilities will result. This situation is already noted in Ref. [1], where the authors are calling for further experimental studies of lifetimes and transition probabilities in bismuth.

In the present work we have performed extensive mea-

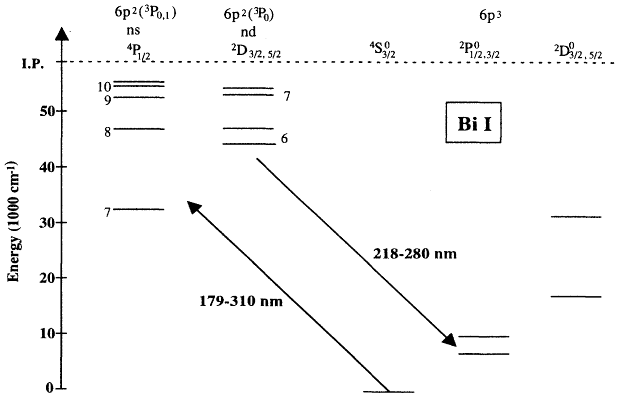

FIG. 1. Partial energy-level diagram for neutral bismuth with relevant transitions indicated.

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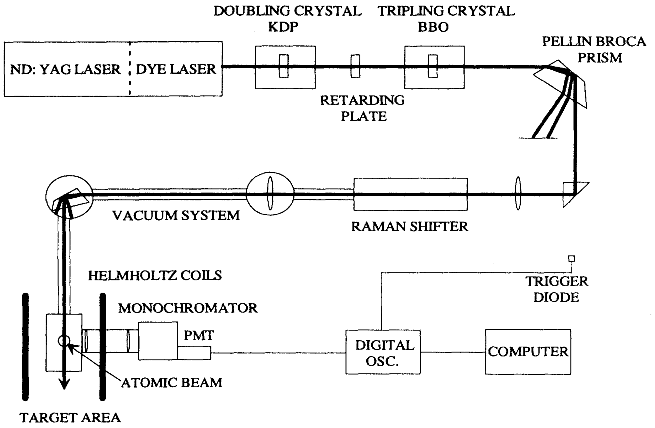

FIG. 2. Experimental setup for time-resolved laser spectroscopy.

surements of natural radiative lifetimes in bismuth using selective laser excitation at short wavelengths. The common way to produce tunable uv-vuv laser radiation is the frequency conversion of visible dye-laser radiation using nonlinear effects in crystals and gases: frequency doubling, tripling, mixing, and Raman shifting. On the vuv laser system at the Lund High Power Laser Facility [13], the lifetimes in Rydberg sequences in a range of atoms [14–17] were investigated by using four-wave mixing (FWM) as the last step of frequency conversion. In the case of bismuth we need to work in the spectral range around 200 nm, and anti-Stokes Raman shifting in molecular hydrogen can be applied as the last step of frequency conversion.

Lifetime measurements were performed for the $6p^27s\,^4P_{3/2}$, $^4P_{5/2}$ and $6p^26d\,^2D_{3/2}$, $^2D_{5/2}$ and $6p^27d\,^2D_{3/2}$, $^2D_{5/2}$ states, and as well in the $6p^2ns\,^4P_{1/2}$ sequence ($n=7-10$). A simplified level scheme for neutral bismuth is shown in Fig. 1 [18]. The measured radiative lifetimes are used to calculate transition-probability data for 26 bismuth lines employing literature values for the branching ratios. By considering all literature data for the bismuth level lifetimes, revised recommended values for transition probabilities are given.

II. EXPERIMENTAL SETUP

The experimental setup used in the present experiments is shown in Fig. 2. The laser light (310–180 nm) that was required to populate the states of interest was produced in different nonlinear processes: frequency doubling, frequency tripling, stimulated anti-Stokes Raman shifting, and stimulated Stokes Raman shifting. In Table I we have listed the frequency conversion schemes used for each state.

A Q-switched neodymium-doped yttrium aluminum garnet (Continuum Model NY82-10) laser (maximum output energy 780 mJ at 532 nm) was used to pump a Continuum Model ND60 nanosecond dye laser that operates on DCM dye (with a maximum output energy of 100 mJ). The output light from the dye laser was first frequency doubled in a potassium-dihydrogen-phosphate (KDP) crystal and then mixed with the fundamental frequency light in a β-barium borate (BBO) crystal to produce the desired uv radiation. In order to effectively achieve mixing, a mechanically compressed crystalline quartz plate was used to rotate the polarizations of the fundamental and the doubled dye-laser beams to obtain parallel polarization vectors before passing the BBO crystal. The generated frequency-tripled radiation was fo-

TABLE I. Presentation of the excitation schemes used, lifetimes obtained, comparison with other experimental data, and recommended lifetimes for Bi I levels.

State	Excitation wavelength (nm)	Wavelength conversion scheme	Radiative Lifetime (ns)		
			Our data	Data of other authors	"Best" data
$6p^27s\,^4P_{1/2}$	306.86	Doubling (D)	5.8(0.4)	4.3(0.2)[a],4.7(1.0)[b],5.66(0.03)[c],5.9(0.2)[d]	5.66(0.03)
$6p\,^27s\,^4P_{3/2}$	222.89	Tripling (T)	5.9(0.8)	7.0(0.2)[a],4.3(0.4)[b],7(2)[e]	6.2(1.0)
$6p^27s\,^4P_{5/2}$	206.23	T	5.7(0.4)	5.1(0.3)[a],5.5(0.5)[b],4.90(0.25)[e],5.25(0.30)[f]	5.3(0.3)
$6p^28s\,^4P_{1/2}$	211.09	T	13.3(0.4)	7.8(0.2)[a]	13.3(0.4)
$6p^29s\,^4P_{1/2}$	191.37	T+first AS	45(3)	13.2(0.5)[a]	45(3)
$6p^210s\,^4P_{1/2}$	183.29	T+second AS	95(8)		95(8)
$6p^26d\,^2D_{3/2}$	227.72	T+first S	30.7(1.4)	27.6(0.5)[a],27(3)[b],28(2)[e]	28.7(1.4)
$6p^26d\,^2D_{5/2}$	223.13	T	4.4(0.6)	3.4(0.6)[a],3.8(1.0)[b]	4.0(0.4)
$6p^27d\,^2D_{3/2}$	196.01	T+first AS	22.8(1.0)		22.8(1.0)
$6p^27d\,^2D_{5/2}$	195.47	T+first AS	16.0(0.6)	7.8(0.3)[a]	16.0(0.6)

[a] Reference [8].
[b] Reference [7].
[c] Reference [10].
[d] Reference [5].
[e] Reference [6].
[f] Reference [9].

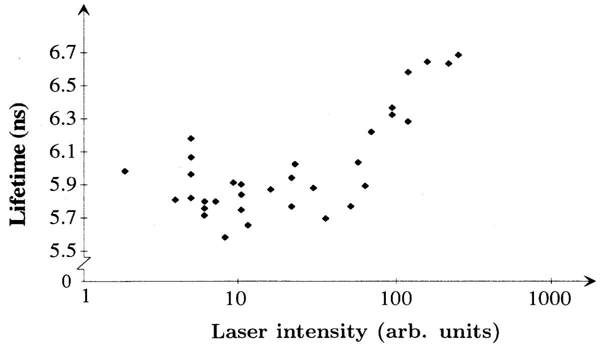

FIG. 3. Evaluated lifetime of the $6p^27s\,^4P_{1/2}$ state as a function of laser intensity.

cused into a high-pressure (10 bar) H_2 gas cell. A CaF_2 Pellin-Broca prism was used to isolate the vuv radiation, which was transported in evaluated tubes to suppress air absorption in the Schumann-Runge molecular oxygen bands. The radiation intersected the atomic beam from a resistively heated oven at right angles and excited the atoms from the ground state to the studied states. Bismuth evaporates to a large extent as molecules, but the atomic fraction was found to be large enough for the present excitation source not to necessitate discharge dissociation [6] or some other atomization method. Fluorescent light collected by calcium fluoride lenses or ordinary quartz lenses (depending on the wavelength of the fluorescent light) was detected at right angles to both the laser and atomic beams using a photomultiplier tube (Hamamatsu R1220) preceded by a vacuum monochromator (Acton Model VM 502). The data acquisition and evaluation were performed using a Tektronic Model DSA 602 digital oscilloscope and a personal computer.

Although vuv radiation can be produced either by using stimulated Raman shifting or four-wave mixing methods, the former method is the most effective one for wavelengths above about 180 nm. For shorter wavelengths the resonant FWM method has to be used to efficiently produce vuv light.

III. MEASUREMENTS AND RESULTS

In order to obtain reliable lifetime values using time-resolved laser spectroscopy, several precautions must be taken. A strong magnetic field had to be applied to wash out any Zeeman quantum beats from hyperfine structure levels. For any studied level, we performed measurements on as many different decay branches as possible to make sure that we detected the right fluorescence, especially in view of the possibility of molecular bismuth excitation. To make sure that the lifetimes were not affected by radiation trapping and collisions, we changed the atomic density by about two orders of magnitude (the atomic beam was produced by thermal heating of metallic bismuth in an oven, the temperature of which was monitored by a thermocouple).

For short-lived states, the laser pulse was recorded to allow deconvolution calculations on the experimental curve to obtain the true exponential decay. One prerequisite for the deconvolution procedure is that the laser intensity is kept low enough to avoid transition saturation. Figure 3 shows the evaluated lifetime of the $6p^27s\,^4P_{1/2}$ state as a function of the laser intensity, ob-

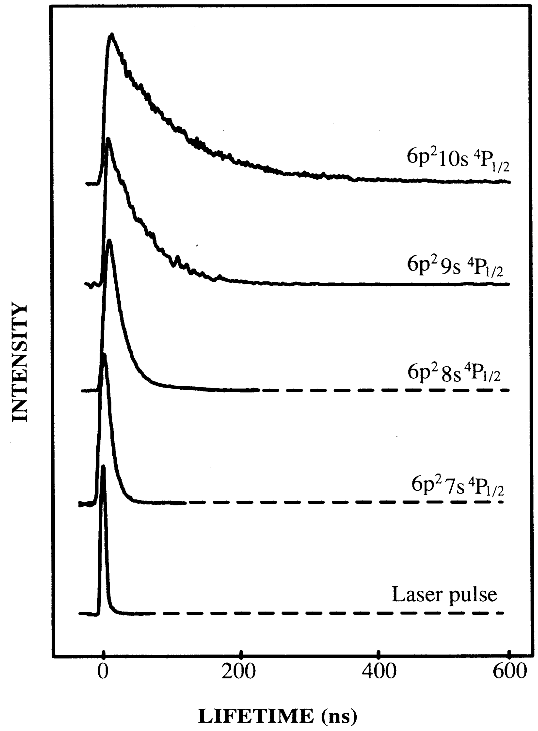

FIG. 4. Recordings of the laser pulse and the time-resolved laser fluorescence in the $6p^2ns\,^4P_{1/2}$ sequence of neutral bismuth.

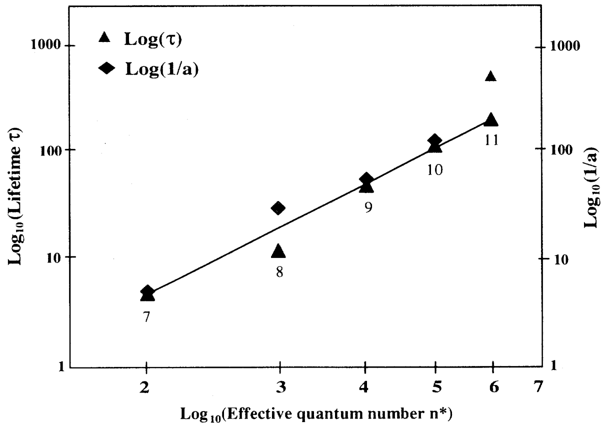

FIG. 5. Lifetimes and inverse hyperfine-structure constants in the $6p^2ns\,^4P_{1/2}$ sequence of neutral bismuth versus the effective quantum number n^* on log-log scales. (▲ are experimental lifetime data (in ns), ◆ are inverse values of the hyperfine-structure constant a (in 10^{-3} cm^{-1}). The straight line shows an n^{*3} dependence fitted for $n=7$.

TABLE II. Comparison of our data and "best" values (ns) with theoretical results for the lifetimes of $6p^27s\ ^4P_{1/2,3/2,5/2}$ state. DV: dipole-velocity approximation, DL: dipole-length approximation.

			Theory					
	Data		Ref. [3]	Ref. [1]		Ref. [2]		
State	Present	"Best"	DL	DV	DL	DV	DL	$(\mathrm{DV}\times\mathrm{DL})^{1/2}$
$6p^27s\ ^4P_{1/2}$	5.8(0.4)	5.66(0.03)	5.7	9.1	6.0	7.1	4.1	5.4
$6p^27s\ ^4P_{3/2}$	5.9(0.8)	6.2(1.0)	4.2	7.7	5.3	8.1	4.5	5.9
$6p^27s\ ^4P_{5/2}$	5.7(0.4)	5.3(0.3)	10.9	5.7	4.2	7.1	4.0	5.3

tained by deconvolution of the recorded decay curve with the laser pulse. We observe that the lifetime is intensity independent when the laser intensity is low enough. For "long-lived" states, the lifetimes were obtained by fitting the experimental curve to an exponential for times late enough (about 10 ns) to be outside the duration of the laser pulse. We used both procedures for the $6p^28s\ ^4P_{1/2}$ level and obtained the same lifetime value, 13.3 ns. For the more long-lived states we then only used the simpler exponential fitting procedure.

Figure 4 shows recordings of the time-resolved laser-induced fluorescence in the $6p^2ns\ ^4P_{1/2}$ sequence of neutral bismuth. For each level about 30–40 fluorescence decays, each obtained by the signal averaging of many individual transients, were recorded at different experimental conditions, and arithmetical mean values of the data obtained are given in Table I. Error bars are taken as two standard deviations. Possible systematic shifts are not included in error bars, but we tried to avoid such shifts by finding the appropriate experimental conditions.

Our lifetimes and inverse hyperfine-structure constants a from literature [20] (in cm^{-1}) in the $6p^2ns\ ^4P_{1/2}$ sequence of neutral bismuth are plotted versus the effective quantum number n^* on a log-log scale in Fig. 5. The straight line shows an n^{*3} dependence fitted for $n=7$. We note that it seems there is a perturbation of the $6p^28s\ ^4P_{1/2}$ state manifested in the lifetime, as well as in the hyperfine-structure data.

TABLE III. Absolute transition probabilities for 26 Bi I lines ($10^6\ \mathrm{s}^{-1}$).

	Wavelength	Transition probability ($10^6\ \mathrm{s}^{-1}$)		
Upper level	(nm)	Data in Ref. [12]	Present	"Best"
$6p^27s\ ^4P_{1/2}$	306.9	207	163	167
	472.4	11.7	9.2	9.4
$6p^27s\ ^4P_{3/2}$	222.9	89.1	92	88
	298.9	55.1	57	54
	339.8	18.1	18.8	17.9
	431.0	1.6	1.7	1.6
$6p^27s\ ^4P_{5/2}$	206.2	98.6	89	96
	269.8	6.4	5.8	6.2
	302.6	88.4	80	86
$6p^28s\ ^4P_{1/2}$	211.0	90.5	53	53
	278.1	30.9	18.1	18.1
	388.8	6.9	4.1	4.1
$6p^26d\ ^2D_{3/2}$	227.7	24.5	22	23.5
	307.8	3.5	3.1	3.3
	351.2	6.8	6.1	6.5
	449.4	1.5	1.3	1.4
$6p^26d\ ^2D_{5/2}$	223.1	260	213	234
	299.4	16.1	13.2	14.5
	340.4	1.6	1.4	1.5
$6p^27d\ ^2D_{3/2}$	196.0	352[a]	15.4	15.4
	252.5	195[a]	8.6	8.6
	281.0	306[a]	13.4	13.4
	340.6	147[a]	6.4	6.4
$6p^27d\ ^2D_{5/2}$	195.5	120	58.6	58.6
	251.6	4.3	2.13	2.13
	279.9	3.6	1.75	1.75

[a] Relative values calculated on the basis of $\tau=1$ ns.

For the $6p^2 11s\ ^4P_{1/2}$ state, the excitation wavelength is 179 nm. To efficiently produce this vuv radiation, the resonant four-wave mixing scheme had to be used [15]. Because the fluorescence was very weak, an interference filter was used instead of a monochromator in the detection system, allowing other fluorescence as well as the desired one to reach the detector. The recorded decay curve included two exponentials; after evaluation two lifetimes [155(15) and 500(100) ns] were obtained. According to the studies of Rydberg series of energy levels in bismuth [19], it seems that there is no perturbation in this state. From Fig. 5 we see that the value 155 ns for the lifetime of the $6p^2\ 11s$ state fits well to an n^{*3} dependence for an unperturbed sequence, and thus the lower of the two values obtained (and indicated in Fig. 5) is the correct one.

For bismuth, the coupling scheme deviates considerably from the pure *LS* type, so excitation from the ground quartet state to doublet states, not matching *LS* selection rules, is possible. In this way the lifetimes of the $6p^2nd\ ^2D_{3/2,5/2}$ ($n=6,7$) states have been measured, by using direct laser excitation from the ground state.

Table I shows the lifetimes that we have measured and previous data. As can be seen from the table, disagreements exist for certain lifetimes obtained by different methods. We think that for the early beam-foil spectroscopy [7] and pulsed electron excitation experiments [8], cascade decays and collisions might have influenced the data. The clear deviation from the delayed-coincidence laser excitation data for the $6p^27s\ ^4P_{1/2}$ state would suggest this. The lifetimes deduced from the Hanle method [6] are somewhat dependent on certain assumptions, such as hyperfine structures and spectral intensity distribution of the excitation source. The Hanle signal for ^{209}Bi consists of a number of Lorentzians with different halfwidths and with weights that depend on the profile of the exciting spectral line. Thus, these weights are influenced by the running conditions of the discharge lamp. A special problem with Hanle-effect data exists for the $6p^26d\ ^2D_{5/2}$ state, where an obviously wrong lifetime estimate [$\tau=(1-2.5)$ ns, not included in the table] was made assuming certain hyperfine-structure conditions, which later measurements have proven to be inaccurate [21]. Our present method of time-resolved laser spectroscopy circumvents these problems. It is worth noting that for the lifetime of the $6s^27s\ ^4P_{1/2}$ state, there is a good agreement between our value and the one obtained by using an accurate single-photon counting delayed-coincidence technique [10].

In Table I we have included recommended "best" lifetime values considering our data and previous ones. For levels where one experiment can clearly be considered to be "best," we recommend it, but in other cases a mean weighted value from the different results is recommended. Values obtained using nonoptical excitation methods [7,8] have been given only half weight. In calculating the best values, no further weighting, reflecting the error bars given by the authors, has been performed, since experience shows that error-bar estimations are frequently unreliable.

A comparison of our data and the "best" data with the results of theoretical calculations [1–3] can only be performed for three states, as shown in Table II. We find a good agreement between experimental data and the mean geometrical value of the dipole-length and dipole-velocity approximations in the semiempirical calculation performed with the Optimized Hartree-Fock-Slater method [2]. Also we see that the conclusion drawn by Bieron and Migdalek in [1] concerning better agreement between their dipole-length approximation (DL) result and experiment is not clear.

Using our lifetime values in combination with branching ratios from literature [12], modified absolute transition probabilities for 26 lines were calculated, as shown in Table III. We also give "recommended" values calculated from the "best" lifetime values listed in Table I.

ACKNOWLEDGMENTS

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