Transition probabilities in neutral barium

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We present emission measurements on a hollow-cathode discharge containing barium that were taken with the aid of a Fourier-transform spectrometer (FTS). We have determined the branching fractions for ten upper levels of the neutral barium atom. In the case of the resonance level $6s6p\ ^1P^\circ_1$, we had to augment our FTS measures with literature data that had recently been obtained by use of different laser-excitation techniques. Using four published lifetimes and also through combining our emission measurements with relative absorption data from the literature, we could convert the branching fractions of eight upper levels into transition probabilities. The resulting A values (with accuracies ranging from 1% to 60%) give support to the correction of earlier literature data, recommended by Jahreiss and Huber [Phys. Rev. A 31, 692 (1985)].

I. INTRODUCTION

As is the case with many other atomic species, the lifetimes of numerous barium levels have been measured, yet branching fractions[1,2] needed to convert these lifetimes into spectroscopically useful transition probabilities are not available. In particular, the branching fractions required for converting the lifetime of the resonance level $6s6p\ ^1P^\circ_1$ (i.e., the upper level of the 553.5-nm Ba I resonance line, cf. Fig. 1) are incomplete. Results on the branching ratio between the resonance line and all the infrared transitions to metastable levels are available,[3–8] but to our knowledge, there are no measurements of the branching ratios between the infrared lines $6s5d\ ^3D_{1,2}, ^1D_2$–$6s6p\ ^1P^\circ_1$ at 1.11, 1.13, and 1.50 μm, respectively. Theoretical data,[9–13] as well as experimental indications[14–17] given in the literature on the relative photon flux in these latter lines (which have also been observed in stimulated emission[18–21]), are contradictory.

Furthermore, a few years ago it was suggested that the transition probabilities for the neutral Ba atom[22] (that had been critically selected and compiled in 1969) undergo a major revision: The transition probabilities for most lines with excited lower levels were found to be too high by a factor of 2 approximately. A set of correction factors of the order of 0.5 to be applied to some of the data compiled in Ref. 22 has been recommended,[14,18] and the resulting transition probabilities were found to be in general agreement with more recent oscillator-strength and lifetime data. Most recently, however, questions regarding the assumptions made in Ref. 14 have been raised.[23]

We therefore have recorded radiometrically calibrated spectra of a Ba hollow-cathode discharge in the wavelength range 320 nm–3.5 μm by use of a Fourier-transform spectrometer (FTS).[24–26] We could thus determine branching fractions for nine levels and branching ratios for the infrared transitions of the upper level ($6s6p\ ^1P^\circ_1$) of the resonance line. Upon augmenting these latter branching ratios with results from several independent laser-excitation experiments,[3–6] we have obtained the branching fractions for the resonance level $6s6p\ ^1P^\circ_1$ as well. Although only four of ten upper levels concerned had measured lifetimes (cf. Fig. 1), we could—through combining our emission measures with absorption data from the literature,[22] i.e., by use of the Ladenburg method[27–29]—derive the transition probabilities for the lines originating in eight upper levels.

II. MEASUREMENTS

The branching fractions and ratios were obtained from two barium hollow-cathode spectra that have been recorded with the McMath Fourier-transform spectrometer at the U.S. National Solar Observatory on Kitt Peak.[24–26] As a light source we used a hollow-cathode lamp based on a design developed by Danzmann and Kock.[29] The hollow cathode, which could be inserted into the lamp, was a 50-mm-long copper cylinder with an inner diameter of 3 mm. BaH_2O_2 powder was introduced into the hollow cathode as a suspension in acetone, evenly distributed on the walls, and dried off by continuously rolling the cathode over a planar surface.[30] The source was run with argon at 0.35 torr as carrier gas and at currents of 0.8 and 1.2 A.

The observed wavelengths ranged from 320 nm to 3.5 μm. To cover this range, the two outputs of the FTS (Refs. 24–26) had different detectors, namely, a 1-cm-diam. uv diode (United Detector Technology Corp.) and a LN_2-cooled InSb detector. The maximum path length difference between the two interferometer beams was $\Delta = 24.2$ cm, and the spectra were sampled at intervals of 0.030 cm^{-1}. To improve the signal-to-noise ratio, each spectrum was built up as a sum over four scans, each of 7-min duration.

The relative radiometric calibration of the FTS and the source optics was obtained with the aid of the Ar I and Ar II branching ratios by Adams and Whaling.[31,32] Our calibration extends from 320 nm up to 2.5 μm and has an uncertainty ranging from 5% to 10%. As wave-number standards, we used the values for Ar I and Ar II, given by

Norlén,[33] and for line identification we used the data published by Moore[34] and Palenius.[35]

III. DATA REDUCTION

The data points in a FTS spectrum represent the intensity per constant wave-number interval, which is proportional to the photon flux (in that wave-number interval). Given optically thin conditions, the area under the profile of a transition between two levels is thus proportional to the number density of the atoms in the upper level and to the transition probability, the constant of proportionality being the radiometric efficiency of the FTS and of the source optics at the wave number of the transition.

The area under a profile was determined by numerical integration in two different ways: In the first instance, we integrated the intensity over a wave-number range that included the line profile as well as the background on both sides of the profile, and plotted the value of the integral versus the wave number of its upper limit. The resulting plot thus had a small mean slope in the background parts (reflecting the deviation of the local background from the zero-intensity level), and a much steeper slope within the range of the profile. The vertical distance covered by the steep part of the plot could be taken as a measure of the area under the profile. This procedure automatically provided the background correction in the immediate vicinity of the line and also gave an estimate of the uncertainty stemming from the choice of the integration limits.

In an alternative procedure we calculated separate integrals for the line and for background regions on both sides of the line. The wave-number ranges of the integrals were not necessarily contiguous. We then computed a mean background value of the data points in the background regions on both sides of the line and subtracted this value from the data points belonging to the integral covering the profile. The standard deviation of the mean background value was also determined in this second procedure; it turned out to be negligible in most cases.

Thus we obtained two photon fluxes belonging to the same transition from each of the two spectra. We combined these four intensity measurements of the same line, which had somewhat different uncertainties, into a weighted mean value for calculating the branching fractions.

By comparing the branching ratios from spectra with different currents, we could evaluate effects from optical thickness in the lines in question. Whereas self-absorption in transitions between high-lying levels was less probable, special care had to be taken regarding transitions into the ground state $6s^2\,{}^1S_0$. Indeed, the resonance line showed an excessive relative width $\delta\sigma/\sigma$ as compared with the other lines and could thus immediately be recognized as exhibiting self-absorption. None of the other transitions involving the ground state showed an enhanced width.

IV. RESULTS AND DISCUSSIONS

Figure 1 shows all the energy levels of neutral barium up to the level $6s7p\,{}^1P^\circ_1$, which is the highest level

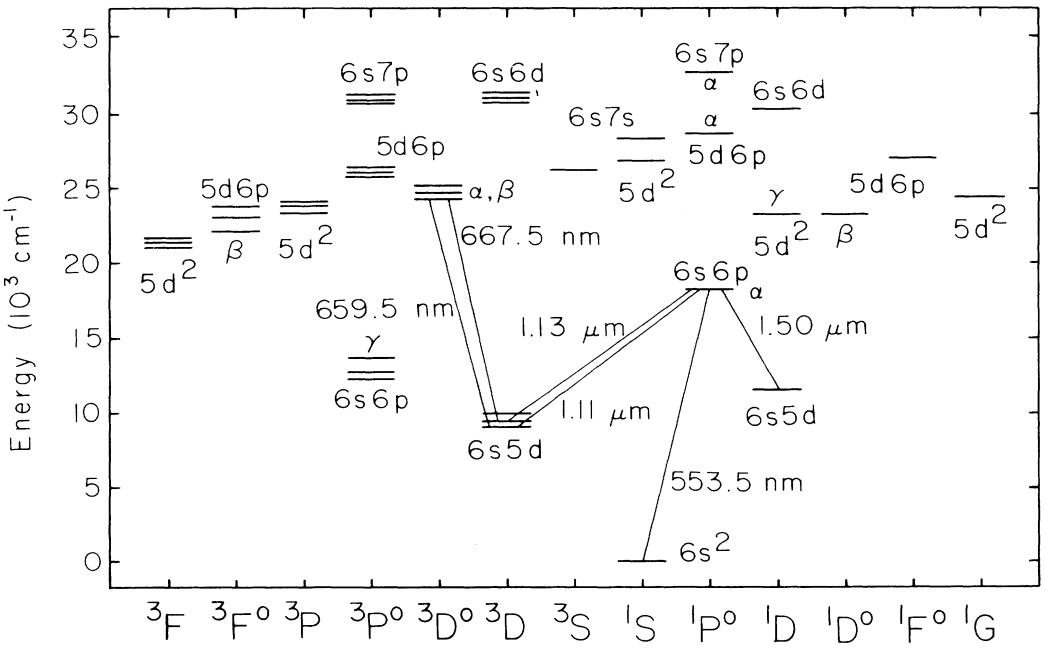

FIG. 1. Relevant energy levels of Ba I. The allowed radiative transitions from the resonance level are indicated. For lines originating in levels designed by Greek letters, we present branching fractions. The fractions of some of these levels were converted to A values by either lifetimes (α) or the Ladenburg method (β). In the latter case, the branching fractions were put onto the absolute transition-probability scale using A (659.5 nm) and/or A (667.5 nm); the corresponding transitions are also indicated. For levels indicated by γ, only branching fractions are given. The energy spacing within the terms is not to scale.

TABLE I. Branching fractions and transition probabilities from levels with known lifetimes compared with literature data.

Upper level	Lifetime (ns)	Lower level	σ (cm^{-1})	λ[b] (nm)	Branching[c] fraction	Transition probabilities[a] (10^E sec^{-1}) Experimental Here	Ref. 14[d]	Ref. 9	Theoretical Refs. 10,11	Ref. 13	E
$6s\,6p\ ^1P_1^\circ$	8.37±0.08[e]	$6s^2\ ^1S_0$	18060.26	553.5	0.9966 (0.2)[f]	1.19±0.01[f]	1.19	1.24	1.33	1.23	8
		$6s\,5d\ ^1D_2$	6664.88	1500.0	0.0025 (15)[f]	3.0±0.5[f]	≤1.7[g]	0.46	1.9	2.8	5
		$6s\,5d\ ^3D_2$	8844.75	1130.3	0.0009 (25)[f]	1.1±0.3[f]		1.2	1.6		5
		$6s\,5d\ ^3D_1$	9026.28	1107.6	<0.000 08[f]	<1.0±0.3[f]		1.2	0.041		4
$5d\,6p\ ^1P_1^\circ$	12.17±0.09[h]	$6s^2\ ^1S_0$	28554.26	350.1	0.43 (9)	3.5±0.3	3.0	4.6	2.0	2.5	7
		$6s\,5d\ ^1D_2$	17158.88	582.6	0.55 (7)	4.5±0.3	≤3.2	3.5	2.4	4.3	7
		$5d^2\ ^1D_2$	5492.20	1820.3	0.014 (19)	1.2±0.2	20[i]				6
		$6s\,5d\ ^3D_2$	19338.74	517.0	0.0011 (50)	9.0±4.5		1.5			4
		$5d^2\ ^3P_2$	4635.32	2165.8	0.0032 (50)	2.6±1.3					5
		$6s\,5d\ ^3D_1$	19520.22	512.1	<0.0004	<3.3±1.0		2.3			4
		$5d^2\ ^3P_1$	5074.25	1970.2	<0.0008	<6.6±2.0					4
		$5d^2\ ^3P_0$	5345.15	1870.3	<0.0006	<4.9±1.5					4
		$5d^2\ ^3F_2$	7620.22	1311.9	<0.0006	<4.9±1.5					4
		$5d^2\ ^1S_0$	1796.9	5563.6							
		$6s\,7s\ ^1S_0$	324.18	30839							
		$6s\,7s\ ^3S_1$	2393.97	4176.0							
$6s\,7p\ ^1P_1^\circ$	13.2±0.4[j]	$6s^2\ ^1S_0$	32547.08	307.2	≥0.54±(50)	≥4.1±2.1	4.2	4.4	5.2		7
		$6s\,5d\ ^1D_2$	21151.69	472.6	0.44 (27)	3.3±0.9	≤3.4	3.1	3.4		7
		$5d^2\ ^1D_2$	9485.02	1054.0	0.024 (36)	1.8±0.7			3.8−13[k]		6
		$5d^2\ ^1S_0$	5789.7	1726.7	<0.004	<3.0±0.9			0.15−3.7[k]		5
		$6s\,7s\ ^1S_0$	4317.00	2315.8	<0.005	<3.8±1.1					5
		$6s\,5d\ ^3D_1$	23513.09	425.2	<0.002	<1.5±0.5		0.079			5
		$6s\,5d\ ^3D_2$	23331.56	428.5	<0.005	<3.8±1.1		6.3			5
		$5d^2\ ^3F_2$	11613.04	860.9	<0.004	<3.0±0.9					5
		$5d^2\ ^3P_0$	9338.00	1070.6	<0.003	<2.3±0.7					5
		$5d^2\ ^3P_1$	9067.07	1102.6	<0.005	<3.8±1.1					5
		$5d^2\ ^3P_2$	8628.14	1158.7	<0.003	<2.3±0.7					5
		$6s\,7s\ ^3S_1$	6386.79	1565.3	<0.003	<2.3±0.7					5
		$6s\,6d\ ^1D_2$	2310.22	4327.3							
		$6s\,6d\ ^3D_1$	1851.48	5399.6							
		$6s\,6d\ ^3D_2$	1796.41	5565.2							
$5d\,6p\ ^3D_1^\circ$	17.4±0.5[l]	$6s^2\ ^1S_0$	24192.06	413.2	0.026 (13)	1.5±0.2	1.3	1.5	26		6
		$6s\,5d\ ^3D_1$	15158.07	659.5	0.64 (5)	3.7±0.2	≤3.9	3.6	5.7		7
		$6s\,5d\ ^3D_2$	14976.54	667.5	0.32 (10)	1.8±0.2	≤1.9	2.0	1.0		7
		$5d^2\ ^3F_2$	3258.02	3068.5	0.011 (60)	6.3±3.8					5

TABLE I. (*Continued*).

Upper level	Lifetime (ns)	Lower level	σ (cm^{-1})	λ[b] (nm)	Branching[c] fraction	Transition probabilities[a] (10^E sec^{-1}) Experimental Here	Ref. 14[d]	Ref. 9	Theoretical Refs. 10,11	Ref. 13	E
$5d\,6p\ ^3D_1^\circ$		$6s\,5d\ ^1D_2$	12 796.68	781.3	<0.001	<5.8±1.7		16	200		4
		$5d^2\ ^3P_0$	982.95	10170							
		$5d^2\ ^3P_1$	712.05	14040							
		$5d^2\ ^3P_2$	273.12	36 604							
		$5d^2\ ^1D_2$	1130.00	8847.2							

[a]The transition probabilities are to be multiplied by the powers of ten with the exponents given in the last column of the Table.
[b]Wavelength (in air).
[c]Values in parentheses indicate uncertainties in percent. All the upper limits given are uncertain to within ±30%.
[d]The uncertainties for the values from Jahreiss and Huber (Ref. 14) are estimated to be within 50%, except for the resonance line where the uncertainty lies within 3%.
[e]Reference 36.
[f]Our measurements comprise the branching ratios between the infrared transitions only. The branching fractions listed here are based on a ratio of 290±40 (Refs. 3–6) between the radiative decay rate of the resonance transition and that of the sum over all transitions to metastable levels. Bushaw and Gerke (Ref. 7) deduced a value of 440±40 for the same ratio. With this latter ratio, the transition probabilities to the levels $6s\,5d\ ^1D_2, ^3D_{2,1}$ become $(2.0\pm0.3)\times10^5$, $(7\pm2)\times10^4$, and less than $6\times10^3\ s^{-1}$, respectively; the transition probability for the resonance transition does not increase noticeably (by one part in 8.5×10^2 only).
[g]Based on data from Ref. 8, cf. Appendix.
[h]Reference 37.
[i]Based on data from Ref. 40, cf. Appendix.
[j]Reference 38.
[k]Ranges are given for the calculated transition probabilities by Friedrich and Trefftz.[10]
[l]Reference 39.

TABLE II. Measured branching fractions and transition probabilities deduced from calculated lifetimes by use of the Ladenburg method.

Upper level	Lifetime[b] (ns)	Lower level	σ (cm^{-1})	λ[c] (nm)	Branching[d] fraction	Transition probabilities[a] (10^E sec^{-1}) Experimental Here	Experimental Ref. 22[e,f]	Theoretical Ref. 9	Theoretical Refs. 10,11	E
$5d\,6p\ ^1D_2^\circ$	32±5	$6s\,5d\ ^1D_2$	11 679.03	856.0	0.63 (4)	2.0±0.3		2.2	3.7	7
		$6s\,5d\ ^3D_1$	14 040.43	712.0	0.34 (8)	1.1±0.2	1.2	0.41	1.7	7
		$6s\,5d\ ^3D_2$	13 858.90	721.4	0.002 (29)	6.3±2.1		120	93	4
		$6s\,5d\ ^3D_3$	13 477.87	741.8	0.024 (14)	7.5±1.6	14	6.4	2.6	5
		$5d^2\ ^1D_2$	12.36	808 800						
		$5d^2\ ^3F_2$	2140.38	4670.8						
		$5d^2\ ^3F_3$	1824.17	5480.5						
$5d\,6p\ ^3D_2^\circ$	18±3	$6s\,5d\ ^3D_1$	15 497.55	645.1	0.19 (12)	1.1±0.2	0.62	1.04	0.69	7
		$6s\,5d\ ^3D_2$	15 316.02	652.7	0.54 (7)	3.1±0.6	3.3	2.9	4.5	7
		$6s\,5d\ ^3D_3$	14 934.99	669.4	0.24 (13)	1.3±0.3	1.6	1.9	1.2	7
		$6s\,5d\ ^1D_2$	13 136.15	761.0	0.019 (16)	1.1±0.3		0.94	13.0	6
		$5d^2\ ^3F_2$	3597.50	2779.0						
		$5d^2\ ^3F_3$	3281.29	3046.8						
		$5d^2\ ^3P_1$	1051.53	9507.4						
		$5d^2\ ^3P_2$	612.60	16 319						
		$5d^2\ ^1D_2$	1469.27	6803.3						
$5d\,6p\ ^3F_2^\circ$	34±6	$6s\,5d\ ^3D_1$	13 030.68	767.2	0.50 (6)	1.5±0.28	1.7	3.2	2.7	7
		$6s\,5d\ ^3D_2$	12 849.14	778.0	0.25 (10)	7.4±1.5	7.3	8.3	10.7	6
		$6s\,5d\ ^1D_2$	10 669.28	937.1	0.25 (10)	7.4±1.5		0.48	4.9	6
		$6s\,5d\ ^3D_3$	12 468.11	801.8	<0.0003	<0.9		13	7.4	4
		$5d^2\ ^3F_2$	1130.62	8842.3						
		$5d^2\ ^3F_3$	814.41	12 275						
$5d\,6p\ ^3F_3^\circ$	30±5	$6s\,5d\ ^3D_2$	13 731.92	728.0	0.81 (3)	2.7±0.5	3.0	2.5	4.0	7
		$6s\,5d\ ^3D_3$	13 350.89	748.8	0.18 (12)	6.0±1.2	5.6	4.5	5.4	6
		$6s\,5d\ ^1D_2$	11 552.01	865.4	0.009 (21)	3.0±0.8		6.0	15	5
		$5d^2\ ^3F_2$	2013.40	4966.0						
		$5d^2\ ^3F_3$	1697.19	5890.5						
		$5d^2\ ^3F_4$	1323.74	7552.3						

[a]The transition probabilities are to be multiplied by the powers of ten with the exponents given in the last column of the Table.

[b]Calculated lifetimes by combining data from anomalous-dispersion and emission measurements.

[c]Wavelength (in air).

[d]Uncertainties in percent.

[e]As recommended by Jahreiss and Huber (Ref. 14), all transition probabilities from Ref. 22 with lower levels belonging to the $6s\,5d\ ^3D$ have to be corrected by the factor 0.56. The values given in this column are corrected accordingly.

[f]The uncertainties of the values of Ref. 22 is estimated by the authors to be 50%.

wherefrom radiative decays were studied in this work. Branching fractions and probabilities of the transitions originating in levels with measured lifetimes (marked by α in Fig. 1) are compiled in Table I whereby our branching-ratio measures for the resonance level were converted into branching fractions by use of results from laser-excitation experiments.[3-6] Table II shows additional transition probabilities obtained with the Ladenburg method,[27-29] namely, by linking our relative emission measures to the absolute transition-probability scale by use of relative absorption measures on two suitable lines (cf. Fig. 1) that share a common lower level with lines listed in Table I. Branching fractions for levels whose lifetimes are not yet measured, and that cannot be put onto the absolute scale in the described manner either, are listed in Table III. In Tables I–III we also list calculated values, based on different approximations: Hafner and Schwarz[9] and Bauschlicher *et al.*[13] used a relativistic pseudopotential approach, whereas Friedrich and Trefftz[10] and Trefftz[11] worked with a nonrelativistic multiconfiguration approximation. For completeness, all possible $E1$ transitions (including intercombination lines) stemming from a common upper level are included in these Tables, even if neither an experimental nor a theoretical A value is known.

Transitions outside the radiometrically calibrated range of our spectra were in general excluded from our analysis, because an extrapolation of the intensity calibration would have introduced too large an uncertainty. Strictly speaking, therefore, we list branching ratios rather than fractions. But, even if one assumes a dipole moment for the neglected lines that is as large as that of the strongest decay channel from a given upper level, the corresponding branching fractions are so small (given the $1/\lambda^3$ dependence of transition probabilities) that their influence on the other transition probabilities remains within the experimental uncertainty in most cases. (Exceptions would be the two-electron transitions $6s7s\ ^3S_1-5d6p\ ^1P^\circ_1$ and the intercombination line $6s5d\ ^1D_1-6s6p\ ^3P^\circ_2$ with wavelengths of 4.2 and 4.7 μm, respectively. However, since to our knowledge these lines have not yet been observed, we assume, for the sake of simplicity, that they can be neglected.)

For several lines we give upper limits of the branching fractions. These lines were not observed in our spectra and the stated numbers correspond to the measured background intensities at the transition wave numbers. In computing the branching fractions for a given upper level, we assumed that there was no actual contribution from such transitions. The uncertainty of all the upper limits was estimated to be $\pm 30\%$.

For the upper levels listed in Table I, several lifetime values—measured with different methods—are available in the literature (cf. Ref. 14 for a discussion of these data). To convert our branching fractions into transition probabilities, we selected the most accurate data,[36-39] which all turned out to be lifetimes determined from Hanle-effect measurements.

In the following we shall summarize the specific procedures used in deriving the data presented in the Tables and discuss them, in particular by comparing them with literature values. We start with the results, listed in Table I, for upper levels having measured lifetimes and proceed level by level starting with the resonance level $6s6p\ ^1P^\circ_1$. From our measurements we obtained the branching ratio between the two infrared lines at $\lambda = 1.50$ and 1.13 μm (cf. Fig. 1),

$$A(6s\,5d\ ^1D_2-6s\,6p\ ^1P^\circ_1)/A(6s\,5d\ ^3D_2-6s\,6p\ ^1P^\circ_1) = 2.8\pm 0.8\ .$$

The $^3D_1-{}^1P^\circ_1$ transition at $\lambda = 1.11$ μm is considerably weaker, the corresponding ratio with that transition in the denominator being greater than 30 ± 13.

The transition to the ground state, i.e., the resonance line at $\lambda = 553.5$ nm, turned out to be self-absorbed in our spectra. To complete the branching fractions from this upper level and convert them into transition probabilities, we had to use results from other experiments. Several groups, using different laser-excitation techniques, have measured the ratio between the radiative decay rate of the resonance transition and that of the aggregate transitions to the metastable levels $6s5d\ ^1D_2, {}^3D_{2,1}$.

Measurements of the resonance fluorescence yielded 280 ± 30 (Ref. 3) and 57 ± 11 (Ref. 4). The first value was

TABLE III. Measured branching fractions for levels with unmeasured lifetimes compared with the theoretical results.

Upper level	Lower level	σ (cm^{-1})	λ[b] (nm)	Branching fractions[a] Here	Ref. 9	Refs. 10, 11	Ref. 13
$6s\,6p\ ^3P^\circ_2$	$6s\,5d\ ^3D_3$	3918.19	2551.5	0.78±0.04	0.813	0.798	0.80
	$6s\,5d\ ^3D_2$	4299.22	2325.4	0.19±0.02	0.169	0.185	0.19
	$6s\,5d\ ^3D_1$	4480.75	2231.2	0.031±0.003	0.016	0.015	0.01
	$6s\,5d\ ^1D_1$	2119.36	4717.1		0.002	0.002	
$5d^2\ ^1D_2$	$6s\,6p\ ^1P^\circ_1$	5001.80	1998.7	0.28±0.03	0.12		
	$6s\,6p\ ^3P^\circ_1$	10425.44	958.9	0.38±0.03	0.21		
	$6s\,6p\ ^3P^\circ_2$	9547.32	1047.1	0.34±0.03	0.67		
	$5d\,6p\ ^3F^\circ_2$	997.40	10023				
	$5d\,6p\ ^3F^\circ_3$	114.62	87221				

[a]The published transition probabilities are converted to branching fractions.
[b]Wavelength (in air).

obtained on an atomic beam, and the second value was derived from an experiment using barium vapor in an argon buffer gas. In a comment on this latter experiment, Kallenbach and Kock[5] have pointed out that the ratio of 57 ± 11 should be increased by about a factor of 5 since spin-changing collisions between barium atoms in the resonance level and buffer-gas atoms had strongly populated the level $6s6p\ ^3P_2$ and therefore had increased the apparent decay rate of the resonance fluorescence. The corrected value, 285 ± 55, is in close agreement with the former datum of 280 ± 30 by Lewis *et al.*[3] These two results receive further support by data obtained from electron-impact ionization cross-section measurements on laser-excited Ba atoms, which yielded 300 ± 45 (Ref. 6). Bushaw and Gerke,[7] on the other hand, report a ratio of 440 ± 40, which they obtained in a pump-probe experiment. Finally, Bernhardt *et al.*[8] had deduced a ratio of ≥ 700 from an isotope-separation experiment. Because they had neglected the intercombination transitions to the levels $6s5d\ ^3D_{2,1}$ in the interpretation of their measurements, a reanalysis of their data[8,40,41] is given in the Appendix. This lowers their value to 550 $(+100,-20)$, but does not bring it into the range of the more recent and more direct measurements.

To convert the measured branching ratios of the infrared lines into branching fractions for the resonance level listed in Table I, we chose the mean of the results given in Refs. 3–6,

$$A(6s^2\ ^1S_0-6s6p\ ^1P_1^\circ)/\sum A(6s5d\ ^1D_2,^3D_{2,1}-6s6p\ ^1P_1^\circ) = 290\pm40\ .$$

Given the possibility, however, that Bushaw and Gerke's[7] value of 440 ± 40 might be correct instead, we also mention (in footnote f of Table I) the corresponding alternative values for the transition probabilities. We did not, on the other hand, make use of the corrected value resulting from the isotope-separation experiment.[8] In the absence of uncertainty estimates, the theoretical data for this ratio—variously reported as 430,[9] 380,[10,11] and 600 (Ref. 12)—could unfortunately not be used in evaluating a "best" value.

Regarding the level $5d6p\ ^1P_1^\circ$, we note that the transition probabilities for the lines at $\lambda=350.1$ and 582.6 nm, as deduced from our branching fraction measurements, confirm the correction factors from Jahreiss and Huber,[14] although the upper limit for the latter transition given by these authors seems not to be compatible with our result. The reason is that the respective correction factor given in Ref. 14 depended on a radiative decay rate to the level $5d^2\ ^1D_2$ ($\lambda=1.8\ \mu$m),[40] for which we derive a transition probability that is lower by nearly a factor of 20. A detailed explanation of how this discrepancy between Refs. 14, 40, and our result is resolved is given in the Appendix as well.

Out of the upper level $6s7p\ ^1P_1^\circ$, six spin-allowed and nine intercombination $E1$ transitions are possible. Directly, we observed the lines to the levels $6s5d\ ^1D_2$ ($\lambda=472.6$ nm) and $5d^2\ ^1D_2$ ($\lambda=1.05\ \mu$m). These are the two strongest transitions besides that to the ground state, which, having a wavelength of 307.2 nm, fell outside the range covered by our experiment. In order to be able to list a transition probability for this line nevertheless, we used the fact that, according to Ref. 14, the ratio of the photon flux in the 472.6-nm transition to that in the 307.2-nm line (to the ground state) must be less than $0.81\pm50\%$. This ratio establishes a lower limit for this latter line.

In determining the relative decay rate out of the level $5d6p\ ^3D_1^\circ$ to the level $5d^2\ ^3F_2$ at $\lambda=3.1\ \mu$m, we had to extrapolate the calibration curve. The contribution of this line is small (its transition probability is most likely less than half that for the very weak 413.2-nm line to the ground state) and therefore does not seriously influence the branching fractions of the other transitions. The $^1D_2-^3D_1^\circ$ intercombination line at 781.3 nm was not observed in our spectra, although the theoretical values for this transition are significantly higher than our upper limit. The transition probabilities for the other lines originating in this upper level, however, are in excellent agreement with the A values of Ref. 14 as well as with the values calculated by Hafner and Schwartz.[9]

We also determined branching fractions for six upper levels whose lifetimes are not yet measured. At first sight it would thus appear impossible to put these measurements onto the absolute scale. Yet there are transitions from four of these six upper levels for which transition probabilities—or, in this context oscillator strengths—have been measured by anomalous dispersion.[22,42] These oscillator strengths in turn have been determined relative to those of the 667.5- and 659.5-nm lines, which are listed in Table I and thus have known transition probabilities (cf. Fig. 1). This offers the possibility of putting the transitions out of the four upper levels listed in Table II onto the absolute scale. Lines originating in these upper levels share the lower levels $6s5d\ ^3D_{2,1}$ with the 667.5- and 659.5-nm lines; thus, as already pointed out by Ladenburg,[27–29] a *direct* linking of the transition probability scale can be made, because in this case the anomalous-dispersion data are independent of relative level populations. This enabled us therefore to compute the lifetimes for these four upper levels by use of our measured branching fractions.

The transitions out of the level $5d6p\ ^1D_2^\circ$ were put on the absolute scale by the ratio A (712.0 nm)/A (659.5 nm), derived from anomalous-dispersion measurements,[22] and by use of the value for A (659.5 nm) given in Table I. The resulting transition probability for the 712.0-nm line is in close agreement with the value from Miles and Wiese,[22] corrected according to Ref. 14 (i.e., by multiplication with the factor 0.56). On the other hand, the literature A value of the 741.8-nm transition ($6s5d\ ^3D_3-5d6p\ ^1D_2^\circ$) appears to be still too high by a factor of 2 even after its correction. This remains unexplained, but we note that our transition probability agrees with the theoretical value of Ref. 9 (as in the case for the 865.0-nm line). However, there is drastic disagreement between theory and experiment in the case of the transition $6s5d\ ^3D_2-5d6p\ ^1D_2^\circ$. The lifetimes obtained from theoretical transition probabilities are 36 ns (Ref. 9) and 18 ns (Refs. 10 and 11), respectively. Again the datum of Ref. 9 agrees with the experimentally derived lifetime.

Two possibilities are given to compute the lifetime of

the level $5d6p\ ^3D_2^\circ$. If the link to the absolute scale is made through the lower level $6s5d\ ^3D_2$, i.e., by use of the A value for the 667.5-nm transition given in Table I, the resulting lifetime is 18 ± 3 ns, whereas a link through $6s5d\ ^3D_1$ and the transition at 659.5 nm yields 34 ± 7 ns. The first derived $^3D_2^\circ$ lifetime agrees with that of the $J=1$ level of the same term, 17.4 ± 0.5 ns (cf. Table I), as would be expected for LS coupling. Also, the calculated lifetimes of 17 (Ref. 9) and 13 ns (Refs. 10 and 11) give more support to our first datum; we therefore rejected the second value. Except for A (645.1 nm) to the level $6s5d\ ^3D_1$, our transition probabilities are in good agreement with the corrected results from anomalous dispersion.[22,42]

The computed lifetimes for the level $5d6p\ ^3F_2^\circ$ are 31 ± 5 or 37 ± 8 ns, depending on whether the link is made by use of the 659.5- or the 667.5-nm transition, respectively. The transition probabilities listed in Table II are based on the mean of these two values. Neither of the two results is compatible with the calculated lifetimes from Ref. 9 (24 ns) and from Refs. 10 and 11 (23 ns). In addition, for the 801.8-nm transition the theoretical results lie about a factor of 10 above our upper limit.

The lifetime of the last level listed in Table II, level $5d6p\ ^3F_3^\circ$, was determined by linking the transition $6s5d\ ^3D_2$–$5d6p\ ^3F_3^\circ$ (728.0 nm) through the $6s5d\ ^3D_2$ level, i.e., by use of A (667.5 nm). The resulting value, 30 ± 5 ns, again is supported by the lifetime derived for the preceding upper level in case the assumption of LS coupling is valid. Our datum agrees with the theoretical lifetime of Ref. 9, 33 ns, but disagrees with 21 ns, calculated by the authors of Refs. 10 and 11.

Considering Table III, finally, we note a good agreement between theory and experiment regarding the level $6s6p\ ^3P_2^\circ$. Only the weak infrared line at 2.23 μm is systematically off by a factor of 2 or more. On the other hand, for the level $5d^2\ ^1D_2$, no agreement can be found between the data of Ref. 9 and our results: The theoretical and experimental distribution of the branching fractions among the transitions is different.

V. CONCLUSIONS

We have measured branching fractions for radiative transitions originating in ten upper levels of the neutral barium atom and present 28 absolute transition probabilities for transitions originating in eight of these levels. The absolute scale was established by use of four upper-level lifetimes and by the Ladenburg method,[27–29] i.e., by use of the results of relative anomalous-dispersion measurements that link the absolute scale through common lower levels of the multiplets concerned. We also list the branching fractions for six additional lines belonging to two upper levels, whose lifetimes have not yet been measured. The uncertainties of our data range from 1% to 60%: 7 values have an accuracy better than $\pm10\%$, 13 better than $\pm20\%$, and 11 better than $\pm40\%$. We also report upper limits (to within an uncertainty of $\pm30\%$) for the transition probabilities of 16 additional lines.

To obtain the branching fractions of the resonance level, we combined our emission measurements with results from laser-excitation experiments. Since there are at present irreconcilable differences between some of the laser-excitation data, we recommend transition probabilities that are substantiated by three independent experiments, but present also alternative results based on the datum from a fourth independent laser-excitation method.

Our transition probabilities are in satisfactory agreement with only some of the theoretical values: Several large deviations between previously calculated transition probabilities and our measurements suggest that new calculations are needed. Intercombination lines (i.e., spin-changing transitions) are affected by disagreement most frequently, and the discrepancies exceed a factor of 10 in several instances.

For the upper levels whose lifetimes are known, as well as for the upper levels where we computed lifetimes by use of the Ladenburg method, the resulting transition probabilities confirmed with very few exceptions the correction factors suggested[14] for some of the values of Ref. 22. From this we conclude that an implied assumption made by Jahreiss and Huber,[14] and recently put into question by Kent *et al.*[23]—namely, that there was no appreciable dimer formation during the ionization of dense barium vapor through resonant laser irradiation[18]—is justified.

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APPENDIX

Notes on isotope-separation efficiency measurements

In this appendix we discuss results obtained in laser isotope-separation experiments by Bernhardt *et al.*[8,40,41] First, we briefly sketch the laser deflection method[41] from which the branching ratios

$$\frac{A(6s^2\ ^1S_0-6s6p\ ^1P_1^\circ)}{\sum A(6s5d\ ^1D_2,{}^3D_{2,1}-6s6p\ ^1P_1^\circ)}$$

and

$$\frac{A(5d^2\ ^1D_2-5d6p\ ^1P_1^\circ)}{A(6s^2\ ^1S_0-5d6p\ ^1P_1^\circ)}$$

have been determined[8,40] (cf. Fig. 2). Then we will explain our reinterpretation of these data. The basis for this reinterpretation is already mentioned in Ref. 14, but we now have additional experimental results at our disposal, which make such a reinterpretation more meaningful.

Isotope separation by laser deflection is based on momentum transfer from the photons emanating from a

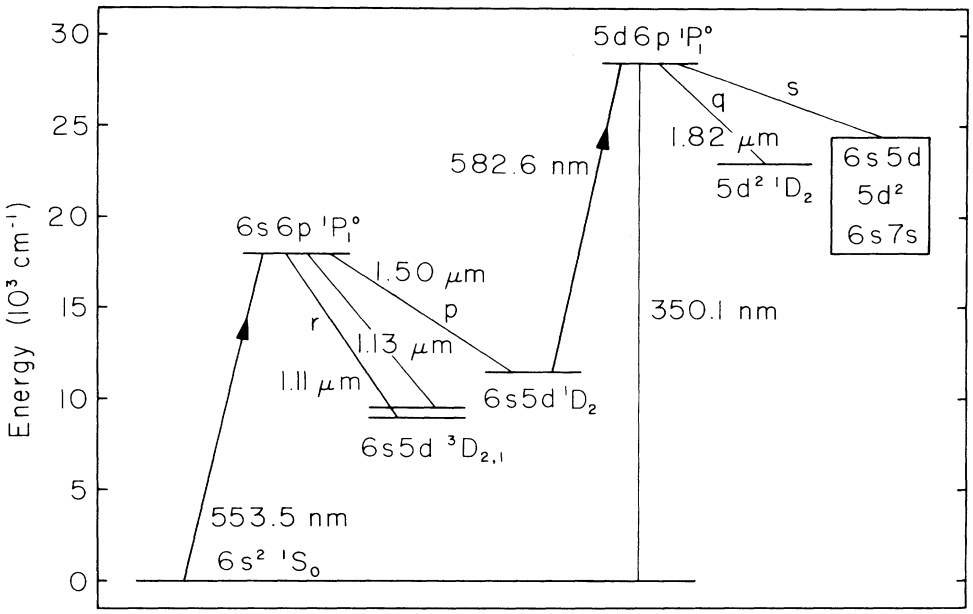

FIG. 2. Laser excitations used for the laser deflection method by Bernhardt *et al.* (Refs. 8, 40 and 41) are indicated by bold arrows. Allowed radiative decay channels from the laser-pumped levels are also indicated. p, q, r, and s refer to branching ratios:

$$p = A(6s\,5d\,{}^1D_2 - 6s\,6p\,{}^1P_1^\circ)/A(6s\,5d\,{}^3D_2 - 6s\,6p\,{}^1P_1^\circ)\,,$$

$$q = A(5d^2\,{}^1D_2 - 5d\,6p\,{}^1P_1^\circ)/A(6s^2\,{}^1S_0 - 5d\,6p\,{}^1P_1^\circ)\,,$$

$$r = A(6s\,5d\,{}^3D_1 - 6s\,6p\,{}^1P_1^\circ)/A(6s\,5d\,{}^3D_2 - 6s\,6p\,{}^1P_1^\circ)\,,$$

$$s = \sum A(6s\,5d\,{}^3D_{2,1}, 5d^2\,{}^3P, {}^3F_2, {}^1S_0, 6s\,7s\,{}^{3,1}S - 5d\,6p\,{}^1P_1^\circ)/A(6s^2\,{}^1S_0 - 5d\,6p\,{}^1P_1^\circ)\,.$$

laser light source (that is tuned to the resonance wavelength of the isotope to be separated) to the atoms in an atomic beam.[41] Atoms undergoing several absorption processes are gaining momentum in the direction of the laser beam and will be continuously deflected outside the main region of the atomic beam. The small probability that after the absorption process an atom in the resonance level decays into a metastable level rather than into the ground state sets a limit to the efficiency of this process: Atoms in metastable states cannot any longer be deflected.

Some of the steps taken by Bernhardt *et al.*[8,40,41] in their experimental procedure can best be discussed in connection with Fig. 2. Atoms pumped to the resonance level by the green laser ($\lambda = 553.5$ nm) can decay to three metastable levels besides the ground state. Bernhardt[41] has shown that after passing through the green pump-laser beam, nearly the entire ground-state population in the atomic beam had been transferred to the terms $6s5d\,{}^{1,3}D$. In another step the $^1D_2$ level was depopulated by a yellow laser ($\lambda = 582.6$ nm); atoms accumulated in this level thus had again, via the level $5d6p\,{}^1P_1^\circ$, a decay channel to the ground state. Again, one transit through the yellow laser beam was sufficient to completely depopulate that metastable level.[41]

In interpreting the results from these two laser-atom interactions (indicated by bold arrows in Fig. 2), Bernhardt *et al.*[8,40,41] have made two assumptions: First, that only one radiative decay channel to a metastable level, namely, to the level $6s5d\,{}^1D_2$ ($\lambda = 1.50$ μm), was available from the resonance level (i.e., $1/p = r = 0$, cf. Fig. 2), and second, that all transitions from the level $5d6p\,{}^1P_1^\circ$ were negligible, except those to the $5d^2\,{}^1D_2$ level ($\lambda = 1.82$ μm) and to the ground state ($\lambda = 350.1$ nm). The latter assumption is justified: $s \leq 0.02 \pm 0.01$ (cf. Table I) leads only to a small correction. Also, our value of $r \leq 0.09 \pm 0.04$ indicates a negligible population of the level $6s5d\,{}^3D_1$, but the branching ratio $p = 2.8 \pm 0.8$ has a large influence, since the spin-changing transition ${}^3D_2 - {}^1P_1^\circ$ is by no means negligible here. The consequence of this we will discuss now.

Branching ratio $q = A(5d^2\,{}^1D_2 - 5d\,6p\,{}^1P_1^\circ)/A(6s^2\,{}^1S_0 - 5d\,6p\,{}^1P_1^\circ)$

By monitoring the intensity of light scattered by the atomic beam from a probe laser tuned to $\lambda = 553.5$ nm, the fraction of atoms that is returned to the ground state after depopulation of the ground state by the green laser and subsequently of the level $6s5d\,{}^1D_2$ by the yellow laser, was determined to be 0.6.[40] Under the assumption that nearly the entire ground-state population is pumped to the level $5d6p\,{}^1P_1^\circ$, i.e., neglecting the branches to $6s5d\,{}^3D$, the result of this measurement was interpreted by Bernhardt *et al.* as

$$1 - q/(1+q) = 0.6 \quad \text{or} \quad q = 0.67\,,$$

Given the relatively strong additional channel for radiative decay from the resonance level to the $6s5d\,{}^3D_2$ level

that is, in fact, available, the branching ratio p has to be included in this equation to give

$$[p/(1+p)][1-q/(1+q)]=0.6 \quad \text{or} \quad q \leq 0.23 .$$

This limit—an upper limit, since the branching ratios r and s were neglected—is significantly lower than the original value.[40] Introducing our uncertainty limits for p in the above formula yields $q \leq 0.11$ and $q \leq 0.30$. We note that there remains an unexplained discrepancy to $q=0.03\pm0.01$ obtained from our emission measurements.

On the other hand, the discrepancy between our value for $A(6s5d\ ^1D_2-5d6p\ ^1P_1^\circ)$ at $\lambda=582.6$ nm and the upper limit given by Jahreiss and Huber[14] (cf. Table I) can now be explained. The correction factor used in Ref. 14 depended on a decay rate $A(5d^2\ ^1D_2-5d6p\ ^1P_1^\circ)$ at $\lambda=1.82$ μm, which was based on the value for $q=0.67$, originally obtained by Bernhardt *et al.*[40] The correction procedure of Jahreiss and Huber for A (582.6 nm), performed by use of our q or the revised q from Bernhardt *et al.*, yield upper limits A (582.6 nm) ≤ 5.1 and 4.5×10^7 s^{-1}, respectively, which both are compatible with $(4.5\pm0.3)\times10^7$ s^{-1}, obtained from our emission measurements.

Branching ratio

$$A(6s^2\ ^1S_0-6s6p\ ^1P_1^\circ)/\sum A(6s5d\ ^1D_2,^3D_{2,1}-6s6p\ ^1P_1^\circ)$$

The value of this branching ratio given in Ref. 8 is based mainly on the interpretation of the three mass-analyzer signals (plotted in Fig. 13 of Ref. 41) which represent the deflected portion of the atomic beam. The signal corresponding to the atomic beam being deflected by the green laser shows 60% of the signal belonging to the undeflected beam entering the mass analyzer. This would indicate that 40% of the ^{138}Ba is being separated from the atomic beam. However, since nearly 100% of the atoms entering the mass-analyzer are in the metastable levels $^{1,3}D$ after being excited by the green laser beam, one has to take into account the increased ionizer efficiency of the mass analyzer to metastable atoms.[41] If the level $6s5d\ ^1D_2$ (by pumping these atoms to the level $5d6p\ ^1P_1^\circ$) is subsequently depopulated by the yellow laser, the mass-analyzer signal is reduced by a factor of 0.7 against that obtained with only the green laser on. Comparison of the mass-analyzer signal obtained with only the green laser on with that taken with both the green and yellow lasers on permits the calculation of the increase of the ionizer efficiency due to the accumulation of atoms in metastable states.

By including the branching ratio p in this calculation and using our value $q=0.03$, the resulting separation-efficiency is lowered to 65% against 70%, based on $1/p=0$ and $q=0.67$.[8] This new value corresponds[8] to a ratio

$$\frac{A(6s^2\ ^1S_0-6s6p\ ^1P_1^\circ)}{\sum A(6s5d\ ^1D_2,^3D_{2,1}-6s6p\ ^1P_1^\circ)}=550 .$$

The resulting small change of the separation-efficiency (or of the branching ratio in question) is due to the almost unchanged net population of atoms in metastable levels entering the mass analyzer, reflecting the fact that the decrease of the number of atoms remaining in the level $5d^2\ ^1D_2$ is nearly compensated by considering the branch to the level $6s5d\ ^3D_2$. Since the branching ratios r and s were neglected, this result represents, strictly speaking, a lower limit for the ratio in question. The limits for minimum and maximum metastable state population (given by the uncertainties of our values for p and q) yield ratios of 530 and 650, respectively.

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[1]Whaling[2] defines the *branching ratio* as $R_{ul'} \equiv A_{ul'}/\sum_l A_{ul}=I_{ul'}/\sum_l I_{ul}$, where $A_{ul'}$ and $I_{ul'}$ are the transition probability and the photon flux, respectively, of the transition from the upper level u to the lower level l' and the sum is taken over all lower levels l to which level u decays. We prefer to use the term *branching fraction* for the case where $\sum_l R_{ul'}=1$. On the other hand, we will use the term branching ratio in those cases where only some of the decays have been measured (i.e., as long as normalization to $\sum_l R_{ul'}=1$ is not possible).

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