Multiconfiguration Dirac-Fock calculations of two electric quadrupole transitions in neutral barium

J. Migdalek* and W. E. Baylis
Department of Physics, University of Windsor, Windsor, Ontario, Canada N9B 3P4
(Received 23 July 1990)

Calculations of electric quadrupole transition probabilities and lifetimes for the $6s5d\ ^3D_2, ^1D_2 - 6s^2\ ^1S_0$ transitions in neutral barium are reported in both the "length" and "velocity" gauges and compared with nonrelativistic multiconfiguration Hartree-Fock results as well as with available experimental data. The lifetime of the $6s5d\ ^1D_2$ state is found to be about $\frac{1}{4}$ s whereas that for the $^3D_2$ state is about 1 min.

The search for new high-efficiency metal-vapor lasers has produced a need for accurate values of the lifetimes of some metastable states. If the lifetime of the metastable state is sufficiently long, it can serve as a reservoir to which ground-state atoms can be pumped and from which, by further excitation, a strong inversion of the principal resonance line can be produced. In particular, in barium the metastable states $6s5d\ ^3D_2, ^1D_2$ decay predominantly by electric quadrupole ($E2$) transitions to the ground state $6s^2\ ^1S_0$. Furthermore, the lifetime of the $^1D_2$ state is required for an evaluation of the transition rate $A(6s6p\ ^3P_1 \rightarrow 6s5d\ ^1D_2)$ by the method of Stark-enhanced decay.[1]

Theoretical and experimental data on metastable states are generally scarce. McCavert and Trefftz[2] performed nonrelativistic multiconfiguration Hartree-Fock (MCHF) calculations of the $6s5d\ ^1D_2 - 6s^2\ ^1S_0$ $E2$ transition probability and found a factor-of-2 difference between the "length" (L) and "velocity" (V) forms of the transition operator. They estimated the lifetime of the $6s5d\ ^1D_2$ state as about 0.5 s, which is four times longer than the value that could be deduced from the measurements of Klimovskii, Minaev, and Morozov.[3] To compute the $E2$ transition probability for the intercombination transition $6s5d\ ^3D_2 - 6s^2\ ^1S_0$, Trefftz[4] used nonrelativistic Hartree-Fock wave functions and a configuration-interaction technique to include spin-orbit coupling. However, this technique only accounts approximately for the spin-orbit interaction, and this interaction is crucial for the intercombination line. A fully relativistic calculation would be preferable.

In the present study, we employ the relativistic multiconfiguration Dirac-Fock (MCDF) method with which we can include both relativistic and electron-correlation effects. Two types of calculation have been performed. In the calculations labeled MCDF-I, the relativistic counterparts of only the $6s5d$ and $5d^2$ configurations are included in the description of the upper $5\ ^3D_2$ and $5\ ^1D_2$ states, whereas in the MCDF-II calculations, the $6p^2$ configuration is also included. In both types of calculation, the ground $6\ ^1S_0$ state is represented by the relativistic counterparts of the $6s^2$, $6p^2$, and $5d^2$ configurations. The percentage compositions of the states given in Table I shows that the con-

TABLE I. Percentage composition of the states $6s5d\ ^3D_2, ^1D_2, 6s^2\ ^1S_0$ in neutral barium. For a description of the computations, see the text.

State	Configuration	MCDF-I	MCDF-II	MCHF
$6\ ^1S_0$	$6s^2_{1/2}$	91.83	91.83	90.8[a]
	$6p^2_{1/2}$	2.78	2.78	
	$6p^2_{3/2}$	4.44	4.44	
	$6p^2$	7.22[b]	7.22[b]	8.2
	$5d^2_{3/2}$	0.34	0.34	
	$5d^2_{5/2}$	0.60	0.60	
	$5d^2$	0.94	0.94	1.0
$5\ ^3D_2$	$6s_{1/2}5d_{3/2}$	64.39	70.25	
	$6s_{1/2}5d_{5/2}$	35.59	29.54	
	$6s5d$	99.98	99.79	99.45[c]
	$5d^2_{3/2}$	0.006	0.02	
	$5d_{3/2}5d_{5/2}$	0.007	0.01	
	$5d^2_{5/2}$	0.011	0.04	
	$5d^2$	0.02	0.07	0.27
	$6p_{1/2}6p_{3/2}$		0.12	
	$6p^2_{3/2}$		0.02	
	$6p^2$		0.14	0.28
$5\ ^1D_2$	$6s_{1/2}5d_{3/2}$	30.35	23.40	
	$6s_{1/2}5d_{5/2}$	55.33	62.15	
	$6s5d$	85.68	85.55	86.86[d]
	$5d^2_{3/2}$	4.18	1.42	
	$5d_{3/2}5d_{5/2}$	3.42	1.12	
	$5d^2_{5/2}$	6.72	2.47	
	$5d^2$	14.32	5.01	7.02
	$6p_{1/2}6p_{3/2}$		6.67	
	$6p^2_{3/2}$		2.77	
	$6p^2$		9.44	6.14

[a]These are the mixing coefficients used in Ref. 2 for calculations of the $5\ ^1D_2 - 6\ ^1S_0$ transition. In calculations of the $5\ ^3D_2 - 6\ ^1S_0$ transition of Ref. 4, the pure (single configuration) $6s^2\ ^1S_0$ state was probably used.
[b]The total contribution of a nonrelativistic configuration usually corresponds to the sum of contributions from several relativistic configurations.
[c]Reference 4.
[d]Reference 2.

TABLE II. Transition energies in cm^{-1} for the $6s5d\ ^3D_2, ^1D_2 - 6s^2\ ^1S_0$ transitions in neutral barium. For a description of the computations, see the text. Corrections are given as follows: A, no Breit or QED corrections; B, Breit interaction included as a perturbation; C, as in B plus QED corrections in a hydrogenic approximation.

Transition	Corrections	MCDF-I	MCDF-II	Experiment
$5\ ^3D_2 - 6\ ^1S_0$	A	12 156.4	12 126.3	
	B	12 099.5	12 070.3	
	C	9 846.9	9 802.9	9 215.518[a]
$5\ ^1D_2 - 6\ ^1S_0$	A	15 958.1	13 676.7	
	B	15 887.2	13 620.9	
	C	13 311.0	11 085.5	11 395.382[a]

[a]Reference 5.

TABLE III. $E2$ transition probabilities in s^{-1} for the $6s5d\ ^3D_2, ^1D_2 - 6s^2\ ^1S_0$ transitions in neutral barium calculated in length (L) and velocity (V) gauges with both experimental (E) and theoretical (T) energies with Breit and QED corrections. For description of the computations, see the text.

Transition	Type	MCDF-I	MCDF-II	MCHF	Experiment
$5\ ^3D_2 - 6\ ^1S_0$	T,L	2.39×10^{-3}	2.29×10^{-2}		
	T,V	2.94×10^{-4}	1.98×10^{-2}		
	E,L	1.72×10^{-3}	1.68×10^{-2}	0.05[a]	
	E,V	2.41×10^{-4}	1.64×10^{-2}		<1[b]
$5\ ^1D_2 - 6\ ^1S_0$	T,L	6.586	3.381		
	T,V	5.542	3.797		
	E,L	3.028	3.880	3.2[c]	
	E,V	3.477	4.124	1.4[c]	8 ± 3[b]

[a]Reference 4.
[b]Reference 3.
[c]Reference 2.

TABLE IV. Lifetimes in s for the $6s5d\ ^3D_2, ^1D_2$ states of neutral barium, calculated in length (L) and velocity (V) gauges with both experimental (E) and theoretical (T) energies with Breit and QED corrections. For a description of the computations, see the text.

State	Type	MCDF-I	MCDF-II	MCHF	Experiment
$6s5d\ ^3D_2$	T,L	418.3	43.6		
	T,V	3404.2	50.6		
	E,L	582.6	59.4	20[a]	
	E,V	4153.0	60.9		>1[b]
$6s5d\ ^1D_2$	T,L	0.152	0.296		
	T,V	0.180	0.263		
	E,L	0.330	0.258	0.31[c]	
	E,V	0.288	0.242	0.70[c]	0.125 ± 0.050[b]

[a]Reference 4.
[b]Calculated from transition probabilities reported in Ref. 3.
[c]Reference 2.

tribution of the $6p^2$ configuration is much larger for the $6\,^1D_2$ state than for the $6\,^3D_2$ state, in which the spin-orbit interaction within the $6s5d$ configuration strongly dominates over the interaction with the remaining configurations.

For both types of calculation, the transition energies have been computed as follows: (A) without the Breit interaction, (B) with the Breit interaction included as a perturbation, and (C) with the Breit interaction plus the QED correction obtained in a hydrogenic approximation. As seen in Table II, inclusion of the $6p^2$ configuration in the $5\,^3D_2$ state (MCDF-II calculations) has virtually no influence on the $6\,^1S_0-5\,^3D_2$ transition energy, but its inclusion in the $5\,^1D_2$ state considerably improves the agreement of the $6\,^1S_0-5\,^1D_2$ transition energy with experiment. The MCDF-II transition energies computed either with or without the Breit interaction but without the QED corrections nevertheless still exceed the experimental data by 20–30 %. The inclusion of QED corrections in the hydrogenic approximation reduces the discrepancy to 3–6 %, with the improvement due almost entirely to an increase in the total energy of the $6s^2\,^1S_0$ ground state. It is difficult to assess whether or not the improvement is fortuitous.

The electric quadrupole transition probabilities and lifetimes were computed using fully relativistic forms of the transition operators in both the length (L) and velocity (V) gauges (see Tables III and IV). Both experimental and theoretical values of the transition energies were used, the latter with both Breit and QED corrections included. The sizable discrepancy found in the MCDF-I calculations between L and V forms of the $5\,^3D_2-6\,^1S_0$ transition probability is almost completely removed in the MCDF-II calculations where the $6p^2$ is included, even though its contribution to the $^3D_2$ state is only 0.14%. The agreement of the L and V forms for the $5\,^1D_2-6\,^1S_0$ transition is good and much better than was obtained in the nonrelativistic MCHF calculations of McCavert and Trefftz.[2] The influence of the $6p^2$ configurations on the $5\,^1D_2-6\,^1S_0$ transition probability is much smaller than for the intercombination line and the large change in the values computed with the theoretical transition energy is almost entirely due to the improvement in the theoretical transition energy mentioned above. The comparison of our fully relativistic results with their nonrelativistic counterparts[2,4] points to the significance of the inclusion of the spin-orbit interaction not only in the diagonalization of the Hamiltonian matrix, but also in the self-consistent-field process itself, as well as to the importance of the residual relativistic effects, even for such a moderately heavy atom as barium.

Our $5\,^1D_2-6\,^1S_0$ electric-quadrupole transition probability of about $4\,s^{-1}$, although larger than the results of McCavert and Trefftz,[2] is still smaller than the experimental data ($8\pm3\ s^{-1}$) of Klimovskii, Minaev, and Morozov.[3] Our value for the intercombination transition $5\,^3D_2-6\,^1S_0$ is about $1.7\times10^{-2}\ s^{-1}$, which is consistent with the results of Klimovskii, Minaev, and Morozov,[3] who were not able to detect any visible absorption of the 10 848-Å line and who estimated its probability to be less than $1\,s^{-1}$. While the present results may be useful in choosing candidates for prospective high-efficiency metal-vapor lasers, we feel that new experiments, with smaller inherent uncertainties than in the absorption method used by Klimovskii, Minaev, and Morozov,[3] would be useful to help assess what further refinements may be desirable in the results presented here.

The authors are greatly indebted to Y.-K. Kim and P. Indelicato for sharing their computer codes with us, and to S. J. Peel for programming assistance. The work was supported by the Natural Sciences and Engineering Research Council of Canada.

---

*Permanent address: Institute of Physics and Department of Computer Science, Pedagogical University of Krakow, PL-30-084 Krakow, Poland.

[1] J. Kwela and A. van Wijngaarden, this issue, Phys. Rev. A **42**, 6360 (1990).

[2] P. McCavert and E. Trefftz, J. Phys. B 7, 1270 (1974).

[3] I. I. Klimovskii, P. V. Minaev, and A. V. Morozov, Opt. Spektrosk. **50**, 847 (1981) [Opt. Spectrosc. (USSR) **50**, 464 (1981)].

[4] E. Trefftz, J. Phys. B 7, L342 (1974).

[5] C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Stand. Ref. Data Ser., Natl. Bur. Stand. (U.S.) Circ. No. 35 (U.S. GPO, Washington, D.C., 1971).