Quasi-metastable quartet levels in alkalilike atoms and ions

S. E. Harris, D. J. Walker, R. G. Caro, and A. J. Mendelsohn

Edward L. Ginzton Laboratory, Stanford University, Stanford, California 94305

R. D. Cowan

Los Alamos National Laboratory, Los Alamos, New Mexico 87545

Received January 5, 1984; accepted February 14, 1984

We describe the properties of a subclass of quartet levels of alkalilike atoms and ions that often retain metastability against autoionization and may have large radiative yields. Gain cross sections for XUV lasers with wavelengths between 20 and 100 nm are given.

It is well known that, in many cases, the quartet level of highest J of a given configuration of an alkalilike atom or ion is metastable against both autoionization and against radiation in the extreme ultraviolet (XUV). This occurs since, irrespective of the extent to which LS coupling holds, there is no doublet level in the configuration to which the quartet level may couple.¹

In this Letter we note the existence of a subclass of quartet levels that, even in heavier elements, often retain relative metastability against autoionization and are radiatively allowed. In elements such as Cs and Ba these levels are candidates for the upper level of XUV lasers. In lighter alkalilike atoms and ions they provide storage levels for store and transfer lasers, which require orders-of-magnitude less transfer laser power than an earlier proposed Li system.²

The distinguishing property of these quasi-metastable levels is that the selection rules on the spin-orbit matrix elements allow nonzero matrix elements only to doublet basis levels, which are themselves prohibited from autoionizing. In second order, through the diagonalization, these levels do develop components of autoionizing doublet levels and therefore do autoionize, but often sufficiently slowly that the branching ratio for XUV radiation remains large.

To illustrate this idea, consider the $2p^53s3p$ configuration of Na. First, the *pure* doublet levels that may not autoionize are $2p^53s3p\ ^2P_{1/2,3/2}$; their doing so would not allow simultaneous conservation of parity and angular momentum. One then tabulates the possible quartet and doublet levels of this configuration: $^4S_{3/2}$, $^4P_{1/2,3/2,5/2}$, $^4D_{1/2,3/2,5/2,7/2}$, $^2S_{1/2}$, $^2P_{1/2,3/2}$, $^2D_{3/2,5/2}$. The pertinent selection rule on the spin-orbit element is $\Delta L = 0, \pm 1$. Therefore, of the possible quartet levels, those that couple only to the nonautoionizing $^2P_{1/2,3/2}$ levels are $^4S_{3/2}$ and $^4D_{1/2}$. We term these levels quasi-metastable.

Table 1 lists the quartet levels of the $2p^53s3p$ configuration and their autoionizing rates as predicted by the atomic-physics code RCN/RCG,³ with only this configuration included. Single and double stars in the left-hand column denote predicted quasi-metastability and metastability, respectively. The nonzero autoionizing rates of the quasi-metastable levels result

from small components of autoionizing doublet levels, which are acquired in second order through the diagonalization. The code expansion of the quasi-metastable $2p^53s3p\ ^4S_{3/2}$ level of Na is

$$\begin{aligned} ^4S_{3/2} = & 0.98\ ^4S_{3/2} - 0.15\ ^4P_{3/2} + 0.07(^1P)^2P_{3/2} \\ & + 0.04(^3P)^2P_{3/2} - 0.001(^1P)^2D_{3/2} \\ & - 0.001(^3P)^2D_{3/2}. \end{aligned} \quad (1)$$

The $(0.001)^2$ components of $^2D_{3/2}$ result in the micro-second-time-scale autoionizing rate. The much larger $(0.07)^2$ component of $(^1P)^2P_{3/2}$ causes no autoionization and leads to a radiative rate of 7.7×10^6 on the transition $2p^53s3p\ ^4S_{3/2} \rightarrow 2p^63p\ ^2P_{3/2}$ at 41.5 nm.

The quasi-metastable $^4D_{1/2}$ level lies higher in the configuration and couples more closely to nearby doublet levels. In second order it acquires a $(-0.014)^2$ component of $(^1P)^2S_{1/2}$, which in turn leads to its autoionizing rate of $2 \times 10^9\ \text{sec}^{-1}$.

Table 2 tabulates the quasi-metastable quartet levels of all s,p,d configurations of the alkalilike atoms and ions. The requirement for quasi-metastability is summarized by $|J - L| = 3/2$; parity and angular momentum must be both even or both odd.

Table 3 tabulates the calculated single configurational autoionizing rate and dominant XUV radiation rate for the lowest-energy quasi-metastable level for the elements of columns I and II. In general, the selection

Table 1. Single Configurational Autoionizing Rates of Quartet Levels in the Sodium $2p^53s3p$ Configuration

Level ^a	Autoionizing Rate (sec ⁻¹)
* $^4S_{3/2}$	6.06×10^5
$^4P_{1/2}$	10.1×10^{10}
$^4P_{3/2}$	4.5×10^{10}
$^4P_{5/2}$	2.67×10^{10}
* $^4D_{1/2}$	0.181×10^{10}
$^4D_{3/2}$	1.25×10^{10}
$^4D_{5/2}$	0.99×10^{10}
** $^4D_{7/2}$	0

^a Single and double stars indicate predicted quasi-metastability and metastability, respectively.

rule on quasi-metastability holds better and is less affected by the inclusion of other configurations for column I than for column II elements. As expected, it also tends to hold better in lighter elements and for low-lying levels.

We have made multiconfigurational code runs on several elements. In sodium, the inclusion of the $2p^5 3s 3p$, $2p^5 3s 4p$, $2p^5 3p 4s$, and $2p^5 3p 3d$ configurations changes the single configurational (Table 1) $2p^5 3s 3p \ ^4S_{3/2}$ autoionizing rate to $4.1 \times 10^5 \text{ sec}^{-1}$ and the $2p^5 3s 3p \ ^4D_{1/2}$ rate to $1.1 \times 10^9 \text{ sec}^{-1}$. In Ca^+ the inclusion of the $3p^5 3d 4s$, $3p^5 4d 4s$, $3p^5 5d 4s$, and $3p^5 3d^2$ configurations changes the $3p^5 3d 4s \ ^4P_{5/2}$ autoionizing rate (Table 3) to $1.03 \times 10^6 \text{ sec}^{-1}$. Ba^+ does particularly poorly. The $5p^5 5d 6s$ and $5p^5 5d^2$ configurations are strongly mixed, and the autoionizing rate of the $^4P_{5/2}$ level can be made to vary between 10^{12} and 10^7 , depending on the choice of the relative average energy of the two configurations.⁴ On the other hand, Cs is relatively insensitive to the relative energy position and has a multiconfigurational autoionizing rate of $7.46 \times 10^7 \text{ sec}^{-1}$.

Radiation in the XUV has been observed and attributed to the $^4S_{3/2}$ and $^4P_{5/2}$ levels in several column I and column II metals by Aleksakhin *et al.*⁵ and by

Fig. 1. Energy-level diagram for 107.5-nm Cs laser.

Table 2. Quasi-metastable Quartet Levels of Alkalilike Configurations

Configuration	Quasi-metastable Levels	Metastable Levels
$p^5 s p$	$^4S_{3/2}, ^4D_{1/2}$	$^4D_{7/2}$
$p^5 s d$	$^4P_{5/2}, ^4F_{3/2}$	$^4F_{9/2}$
$p^5 p d$	$^4S_{3/2}, ^4D_{1/2}, ^4D_{7/2}, ^4G_{5/2}$	$^4G_{11/2}$
$p^5 p^2$	$^4P_{5/2}$	—
$p^5 d^2$	$^4P_{5/2}, ^4F_{3/2}, ^4F_{9/2}$	—

Zhmenyah *et al.*⁶ Also, a single configurational analysis by McGuire⁷ predicts slow autoionizing rates for the $^4S_{3/2}$ levels of Na and Mg^+ .

Table 4 gives the transition wavelength, Doppler width, and gain cross section σ for XUV laser transitions that originate from the lowest quasi-metastable level of each element. The Doppler width is calculated at a

Table 3. Single Configurational Autoionizing and Radiative Rates for Quasi-metastable Column I and Column II Elements

Element	Upper Level	Autoionizing Rate	Radiative Rate	λ (nm)	Lower Level
Na	$2p^5 3s 3p \ ^4S_{3/2}$	6.1×10^5	7.7×10^6	41.5	$3p \ ^2P_{3/2}$
K	$3p^5 3d 4s \ ^4P_{5/2}$	4.6×10^2	3.0×10^6	71.1	$3d \ ^2D_{3/2}$
Rb	$4p^5 5s 5p \ ^4S_{3/2}$	8.6×10^7	2.6×10^7	82.1	$5p \ ^2P_{3/2}$
Cs	$5p^5 5d 6s \ ^4P_{5/2}$	5.1×10^7	4.1×10^7	107.5	$5d \ ^2D_{5/2}$
Mg^+	$2p^5 3s 3p \ ^4S_{3/2}$	9.3×10^4	1.9×10^7	25.6	$3p \ ^2P_{3/2}$
Ca^+	$3p^5 3d 4s \ ^4P_{5/2}$	9.3×10^5	4.1×10^6	52.9	$3d \ ^2D_{5/2}$
Sr^+	$4p^5 4d 5s \ ^4P_{5/2}$	1.4×10^8	5.3×10^7	62.0	$4d \ ^2D_{5/2}$
Ba^+	$5p^5 5d 6s \ ^4P_{5/2}$	2.7×10^9	8.8×10^7	77.1	$5d \ ^2D_{5/2}$

Table 4. Gain Cross Sections of Transitions from Quasi-metastable Levels

Element	Transition	λ (nm)	Doppler Width (cm^{-1})	σ (cm^2)
Na	$2p^5 3s 3p \ ^4S_{3/2} \rightarrow 2p^6 3p \ ^2P_{5/2}$	41.5	1.04	1.6×10^{-16}
K	$3p^5 3d 4s \ ^4P_{5/2} \rightarrow 3p^6 3d \ ^2P_{5/2}$	71.1	0.43	4.4×10^{-16}
Rb	$4p^5 5s 5p \ ^4S_{3/2} \rightarrow 4p^6 5p \ ^2P_{3/2}$	82.1	0.24	9.1×10^{-15}
Cs	$5p^5 5d 6s \ ^4P_{5/2} \rightarrow 5p^6 5d \ ^2D_{5/2}$	107.5	0.15	3.9×10^{-14}
Mg^+	$2p^5 3s 3p \ ^4S_{3/2} \rightarrow 2p^6 3p \ ^2P_{3/2}$	25.6	1.78	8.71×10^{-17}
Ca^+	$3p^5 3d 4s \ ^4P_{5/2} \rightarrow 3p^6 3d \ ^2D_{5/2}$	52.9	0.83	1.72×10^{-16}
Sr^+	$4p^5 4d 5s \ ^4P_{5/2} \rightarrow 4p^6 4d \ ^2D_{5/2}$	62.0	0.45	5.6×10^{-15}
Ba^+	$5p^5 5d 6s \ ^4P_{5/2} \rightarrow 5p^6 5d \ ^2D_{5/2}$	77.1	0.27	2.4×10^{-14}

temperature corresponding to a vapor pressure of 10 Torr.

Figure 1 is an energy-level diagram for a 107.5-nm Cs laser. The $4P_{5/2}$ level will be populated by electron collisions at a peak excitation cross section that Aleksakhin *et al.*⁵ estimate as $5.8 \times 10^{-17} \text{ cm}^2$ and also by charge transfer from the $\text{Cs}^+ 5p^5 6s$ ion. The lower laser level $5p^6 5d \ ^2D_{5/2}$ will also be excited by electron collisions but can probably be emptied by laser excitation to a Rydberg level or to the $\text{Cs}^+ 5p^6$ continuum.

Population in the quasi-metastable levels of the column II elements of Table 4 can be produced by soft-x-ray photoionization^{8,9} of populated valence levels. For example, photoionization of atoms in the $5p^6 5d 6s \ ^3D$ level of Ba will produce $5p^5 5d 6s \ ^4P_{5/2}$ ions with a statistical branching ratio of about 7%. A possible advantage of using column II metals is that the lower laser level is an excited level of the ion rather than of the neutral.

The authors gratefully acknowledge helpful discussions with T. Lucatorto, A. W. Weiss, and P. J. K. Wi-soff.

The research described here was supported by the U.S. Air Force Office of Scientific Research and the U.S. Army Research Office.

References

1. P. Feldman and R. Novick, "Autoionizing states in the alkali atoms with microsecond lifetimes," *Phys. Rev.* **160**, 143 (1967).
2. S. E. Harris, "Proposal for a 207-Å laser in lithium," *Opt. Lett.* **5**, 1 (1980); and J. E. Rothenberg and S. E. Harris, "XUV lasers by quartet to doublet energy transfer in alkali atoms," *IEEE J. Quantum Electron.* **QE-17**, 418 (1981).
3. R. D. Cowan, *The Theory of Atomic Structure and Spectra* (U. California Press, Berkeley, Calif., 1981), Secs. 8-1, 16-1, and 18-7.
4. J. P. Connerade, M. W. D. Mansfield, G. H. Newsom, D. H. Tracy, M. A. Baig, and K. Thimm, "A study of $5p$ excitation in atomic barium. I. The $5p$ absorption spectra of Ba I, Cs I and related elements," *Phil. Trans. R. Soc. London Ser. A* **290**, 327 (1979); S. J. Rose, I. P. Grant, and J. P. Connerade, "A study of $5p$ excitation in atomic barium. II. A fully relativistic analysis of $5p$ excitation in atomic barium," *Phil. Trans. R. Soc. London Ser. A* **296**, 41 (1980).
5. I. S. Aleksakhin, G. G. Bogachev, I. P. Zapesochnyl, and S. Yu. Ugrin, "Experimental investigations of radiative decay of autoionizing states of alkali and alkaline earth elements," *Sov. Phys. JETP* **53**, 1140 (1981).
6. Yu. V. Zhmenyak, V. S. Vukstich, and I. P. Zapesochnyl, "Radiative decay of Na I autoionization states excited in electron-atom collisions," *Pis'ma Zh. Eksp. Teor. Fiz.* **35**, 321 (1982).
7. E. J. McGuire, "The L -MM Auger spectra of Na and Mg," *Phys. Rev. A* **14**, 1402 (1976).
8. R. G. Caro, J. C. Wang, R. W. Falcone, J. F. Young, and S. E. Harris, "Soft x-ray pumping of metastable levels of Li^+ ," *Appl. Phys. Lett.* **42**, 9 (1983).
9. W. T. Silfvast, J. J. Macklin, and O. R. Wood II, "High-gain inner-shell photoionization laser in Cd vapor pumped by soft-x-ray radiation from a laser-produced plasma source," *Opt. Lett.* **8**, 551 (1983).