Importance of an $M2$ Depopulating Channel for a Kr II Metastable State

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An experimental investigation of the radiative lifetime of the metastable $4s^2 4p^4(^3P)4d\ ^4D_{7/2}$ level in Kr II shows an unusual situation regarding the importance of an $M2$ depopulation channel. While the first order $M1$ and $E2$ channels are expected to contribute in a dominant way to the decay, the experimental result, obtained using a laser probing technique on a stored ion beam, $\tau = 0.57 \pm 0.03$ s, is far too short to be due to these channels according to our relativistic multiconfiguration Dirac-Fock calculation. Only if second order contributions to the decay branches (including essentially the $M2$ contribution) are taken into account in the calculations could the unexpected short lifetime be explained.

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In atoms or low-charge-state atomic ions, metastable levels can decay to the ground state via "forbidden" transitions, generally of the magnetic dipole ($M1$) or electric quadrupole ($E2$) types. Radiative rates for $M1$ and $E2$ transitions are usually several orders of magnitude smaller than those for allowed ($E1$) transitions involving levels with a similar energy level separation [1]. As a consequence, radiative lifetimes of metastable levels in these ions are typically in the milliseconds or even in the second range, while a "normal" excited state in a neutral or in a lowly charged ion, decaying via $E1$ transitions, has a lifetime of a few nanoseconds. Many of these forbidden transitions, especially for the light, cosmically abundant elements and their isoelectronic neighbors, are very important for astrophysics because they are observed in low-density plasmas. Indeed, the forbidden transitions can dominate the emission line spectra in the case of dilute astrophysical plasmas where the metastable levels are not collisionally deexcited. Precise measurements of radiative lifetimes for such states in atomic ions are also required for accurate plasma diagnostics because A values of forbidden transitions are less sensitive to saturation effects than those of allowed lines. Experimental studies of lifetimes of metastable levels require a sophisticated technique for the confinement of the ions and the suppression of collisional effects.

Accurate radiative parameters for forbidden transitions of lowly charged ions are difficult to obtain both experimentally or theoretically. In Kr II, theoretical estimates of lifetime values for metastable levels are very sparse [2,3]. In general, such theoretical data are strongly dependent upon the models used for the calculations and, consequently, are very sensitive to small perturbations affecting the wave functions. In addition, theoreticians frequently have to face problems of numerical convergence in the calculations for lowly charged ions. Very large basis sets are also needed for the wave functions, larger than required for satisfactory calculations in highly charged ions, and the use of such large basis sets is frequently prevented or limited by computer constraints.

The ground configuration of Kr II is $4s^2 4p^5$ and the first excited configurations are $4s4p^6$, $4s^2 4p^4 5s$, and $4s^2 4p^4 4d$. In this ion, the $4s^2 4p^4(^3P)4d\ ^4D_{7/2}$ level at 120 209.87 cm^{-1} is metastable and can decay to the $4s^2 4p^4(^3P)5s\ ^4P_{5/2}$ level located at 112 828.27 cm^{-1} via a transition that has both $M1$ and $E2$ depopulation channels (see Fig. 1). Additional possibilities of decay exist to the $4s^2 4p^4(^3P)5s\ ^4P_{3/2}$ or to the $4s^2 4p^4(^3P)5s\ ^2P_{3/2}$ levels at 115 092.012 and 118 474.359 cm^{-1}, respectively, via $E2$ transitions [4].

A relativistic Hartree-Fock (RHF) calculation of the lifetime of this level using Cowan's [1] codes, retaining a set of 20 interacting even configurations within the $n = 4$ and $n = 5$ Layzer complexes and considering an adjustment procedure of the mean energies of the configurations in order to reproduce the lowest observed energy levels, leads to a lifetime value of 9.1 s. Both the $M1$ and $E2$ transition probabilities contribute to the decay: i.e., $A(M1) = 7.853 \times 10^{-3}\ s^{-1}$ and $A_{tot}(E2) = 1.021 \times 10^{-1}\ s^{-1}$. This estimated lifetime value has the same order of magnitude as the lifetimes reported in the literature, e.g., in Li II for the $1s2s\ ^3S_1$ state [5] or in Ba II for the $5d\ ^2D_{3/2,5/2}$ levels [6,7] and which agree well with the theory [2,8,9] when only $E2$ or/and $M1$ decay contributions are considered.

In order to check the validity of the theoretical model, an experiment was performed using the CRYRING storage ion ring at the Manne Siegbahn Laboratory [10].

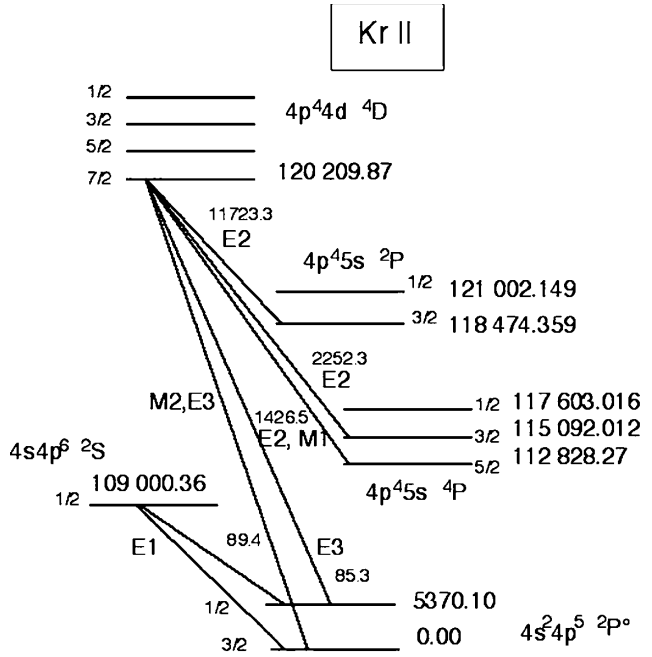

FIG. 1. Kr II: lowest energy levels (energies in cm^{-1}) and wavelengths (in nm) of the depopulating channels of the $4s^2 4p^4 4d\ ^4D_{7/2}$ level to lower energy levels.

Singly charged ions were produced in a low-voltage, hot cathode ion source (MINIS), accelerated by 30 kV and mass separated. The selected ^{84}Kr ions were injected into the storage ring. The stored ion current was about 1 μA. A small fraction of the stored beam consisted of ions in metastable levels that were populated in the ion source. This fraction was used for determination of the lifetime of the metastable level investigated in the present experiment.

The ions were stored at a base pressure less than 10^{-11} Torr. For singly charged ions at a beam energy of 30 keV, the primary process responsible for the ion loss is neutralization by collisions with the rest gas. This process limited the lifetime of the stored ion beam to about 1 min. The decay was monitored with a BaF_2 scintillator detector and a photomultiplier positioned after one of the dipole magnets monitoring neutralized particles and recorded with a multichannel scaler triggered at ion injection.

In the present experiment, we wanted to study the radiative decay of the $4d\ ^4D_{7/2}$ level in Kr II. The lifetime was measured by the laser probing technique [11,12] developed at CRYRING. The population of the metastable level is probed by inducing an allowed transition to a more highly excited level by a laser. The intensity of the prompt fluorescence from the decay of this upper level reflects the population of the metastable level from which the ion was excited. By laser light applied at different times relative to the injection of the ions into the ring, it is possible to record the decay of the ions in the particular metastable level studied.

Beside the decay curve, a number of normalization curves were recorded simultaneously in order to be able to correct for variations in the ion beam intensity, the magnitude of the metastable fraction, and laser stability [11]. These effects were negligible in the present experiment. A special procedure for recording collisional excitation into the metastable level has been developed [11,13]. Such curves were recorded and used to correct the decay curves. This correction changed the extracted lifetime by less than 10%. Special routines for treating data have been developed [11], and the lifetime values were finally extracted by a commercial fitting program (PeakFit).

The lifetime recorded was significantly shorter than 9.1 s, the value that was expected from the calculations including $M1$ and $E2$ channels. There are experimental conditions that may quench the level and cause the lifetime to appear shorter. Careful studies were performed to investigate if that was the case. Collisions are a destructive process that may cause a lifetime shortening. They could both induce direct excitation or deexcitation and neutralization. We have systematically varied the pressure in the ring with a maximum increase of a factor of 8. The results have been plotted in a Stern-Vollmer diagram (Fig. 2), and we conclude that collisional destruction contributes by about 10% at base pressure. Another effect that could shorten the lifetime is mixing of different levels by an external magnetic field. Such an effect was observed once, namely, for the homologous $5d\ ^4D_{7/2}$ in Xe^+ [14] where the field of the bending magnets mixed this level with the $5d\ ^4D_{5/2}$ level [15]. Since the magnetic field that keeps the ion beam in the ring matches the beam energy, it is possible to check the influence of the magnetic field by lifetime measurements at different energies (we used 10, 20, 30, and 40 keV). No systematic variation of the lifetime on the beam energy was observed that should be accounted for. We conclude that the measurements indicate that the radiative lifetime of the $4d\ ^4D_{7/2}$ is 0.57 ± 0.03 s.

This measured lifetime is in contradistinction to the above RHF result. In order to solve this puzzling discrepancy, it was decided to consider in the calculations higher order contributions to the decay branches. It was also decided to perform a full relativistic calculation due to the great sensitivity of the RHF results to the mixing of the levels between states of different LS values and, possibly, to a breakdown of Breit-Pauli approximation in the RHF method. A general formalism for calculating transition probabilities for an electric (E_p) or magnetic (M_p) multipole radiation of order p in a fully relativistic scheme has been given by several authors [16–18], and it provides, in the nonrelativistic limit, the usual formulas corresponding to the length or velocity forms [18,19].

When considering the $4s^2 4p^4(^3P)4d\ ^4D_{7/2}$ level at 120 209.87 cm^{-1}, in addition to the $M1$ and $E2$ channels,

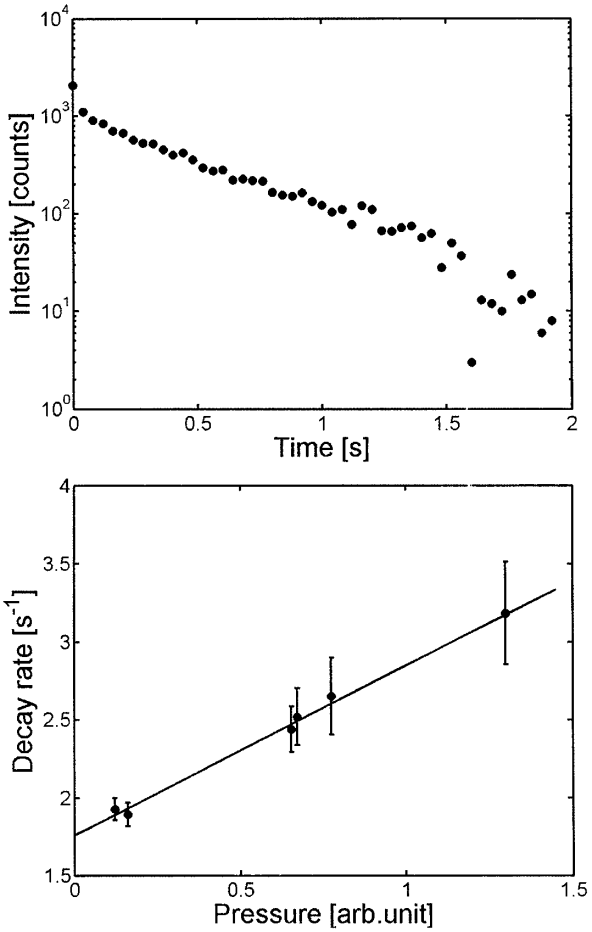

FIG. 2. The upper part of the figure shows one of the decay curves recorded for the $5d\,^4D_{7/2}$ level in Kr II by the laser probing technique. The lower part is a Stern-Vollmer plot showing the observed decay rate of this metastable level as a function of pressure in the storage ring as described in the text. The intercept at zero pressure gives the pure radiative decay rate.

it can also decay to the ground state $4s^24p^5\ ^2P^0_{3/2}$ via an $M2$ transition. Higher order ($E3$) transitions are also possible, and their contribution cannot *a priori* be neglected. The computational procedure used for calculating these higher order contributions to the $4d\ ^4D_{7/2}$ radiative lifetime is the fully relativistic multiconfigurational Dirac-Fock (MCDF) method. We used the GRASP2 package [20], which, although formally unpublished, is in wide circulation through the Internet [21].

This program implements the multiconfigurational Dirac-Fock method [22], which consists in representing the atomic state function (ASF) as a superposition of configuration state functions (CSF) according to

$$\Psi(\alpha \Pi JM) = \Sigma_i c_i(\alpha)\Phi(\beta_i \Pi JM), \qquad (1)$$

where Ψ and Φ are the ASF and the CSF, respectively, Π, J, and M are the relevant quantum numbers, i.e., the parity, the total angular momentum, and its associated total magnetic number, respectively; α and β stand for all the other quantum numbers that are necessary to describe unambiguously the ASFs and the CSFs. The summation in (1) is extended over n_c, the number of CSFs in the expansion. Each CSF is built from antisymmetrized products of relativistic spin orbitals. The coefficients c_i, together with the orbitals, are optimized by minimizing an energy functional. The latter is built from one or more eigenvalues of the Dirac-Coulomb Hamiltonian depending upon the optimization option adopted. Transverse Breit interaction as well as other QED interactions, like vacuum polarization and self-energy, have been added to the Hamiltonian matrix as perturbations.

In order to determine the lifetime of the $4s^24p^4(^3P)4d\ ^4D_{7/2}$ energy level, all the $M1$, $E2$, $M2$, and $E3$ transitions between the lowest levels corresponding to $4s^24p^5\ J = 1/2, 3/2$, to $4s^24p^45s\ J = 3/2, 5/2$,and to $4s^24p^45s\ J = 3/2$ were considered. The calculations were done in three steps. In the first step, we included only the two CSF of the $4s^24p^5$ configuration and performed an average level optimization of the $n = 1$–3 core orbitals along with the $4s$ and $4p$ orbitals. The second step consisted in considering the 39 CSF belonging to the configurations $4s^24p^5$, $4s4p^6$, $4s^24p5s$, and $4s^24p^44d$. The $4s$, $4p$, $4d$, and $5s$ orbitals were optimized minimizing an energy functional built on the lowest nine levels using the EOL (extended optimal level) option [22]. The atomic orbitals were kept fixed to the values of the first step using the configuration interaction option. In the final step, a list of 19 919 CSF was generated from the reference states $4s^24p^5\ J = 1/2, 3/2$, $4s^24p^45s\ J = 3/2, 5/2$, and $4s^24p^44d\ J = 7/2$ by single and double excitations into the $\{4s, 4p, 4d, 4f, 5s, 5p, 5d, 5f\}$ active set of orbitals. All the $n = 4$ and $n = 5$ orbitals were optimized fixing the core to the values of the previous step and minimizing the lowest six levels in the framework of the EOL option. Attempts to further increase the CSF list were prevented by computer limitations. It was also verified that higher-order contributions (i.e., $M3$, $M4$, and $E4$) were negligible (i.e., characterized by A values $<10^{-10}$ s^{-1}).

Table I contains the seven transitions involved in the decay of the $4s^24p^4(^3P)4d\ ^4D_{7/2}$ level along with the calculated wavelengths and Einstein A values. For the $E2$ contributions, both the Coulomb and Babushkin gauges were considered. It is clearly seen that the dominant decay channel is by far the $M2$ transition. It should be pointed out that the transition probabilities reported in this Letter have been calculated using only theoretical energy differences. However, our eigenvalues reproduce the experimental data within 2.5%. Neglecting this channel and considering only the $M1$, $E2$, and $E3$ contributions lead to an MCDF lifetime value of 19 or 32 s, according to the gauge considered. When including the $M2$ contribution, the theoretical lifetime of the $4s^24p^4(^3P)4d\ ^4D_{7/2}$ level is $\tau = 0.94$ s in the Babushkin

TABLE I. Transitions involved in the decay of the $4s^2 4p^4(^3P)4d\ ^4D_{7/2}$ level and MCDF transition rates. The wavelengths and wave numbers are calculated values.

Transition		Type	λ_{MCDF} (nm)	σ (cm^{-1})	A^{a} (s^{-1})
$4s^2 4p^4(^3P)4d\ ^4D_{7/2}$	- $4s^2 4p^5\ ^2P^0_{3/2}$	$M2$	85.3	117 261	1.01
	- $4s^2 4p^5\ ^2P^0_{3/2}$	$E3$	85.3	117 261	9.35(−5)/1.26(−4)
	- $4s^2 4p^5\ ^2P^0_{1/2}$	$E3$	89.4	111 910	2.69(−5)/3.54(−5)
	- $4s^2 4p^4(^3P)5s\ ^4P_{5/2}$	$M1$	1426.5	7010	9.21(−5)
	- $4s^2 4p^4(^3P)5s\ ^4P_{5/2}$	$E2$	1426.5	7010	5.17(−2)/2.90(−2)
	- $4s^2 4p^4(^3P)5s\ ^4P_{3/2}$	$E2$	2252.3	4440	1.62(−3)/2.19(−3)
	- $4s^2 4p^4(^3P)5s\ ^4P_{3/2}$	$E2$	11 723.3	853	8.29(−8)/5.74(−7)

[a] $a(b)$ stands for $a \times 10^b$. $a(b)/c(d)$ means Babushkin value/Coulomb value.

gauge and $\tau = 0.96$ s in the Coulomb gauge. The remaining discrepancy between the two gauges' results indicates that the calculations could still be refined, but this was not possible here in view of the limits, which were imposed by the computer. It should also be noted that inserting the experimental excitation energy into the calculations directly increases the transition rate by more than 10%, which brings it closer to the observed value. The importance of the correlation on the $M2$ rate must be emphasized: a monoconfigurational Dirac-Fock calculation leads to a transition energy of 140 840 cm^{-1} ($\approx$15% greater than the experimental value) and a transition probability of 0.282 s^{-1} (a factor of ≈ 4 smaller than the MCDF result reported in Table I).

The lifetimes deduced from the MCDF calculations are longer—but nevertheless in reasonable agreement — than the experimental measurement, i.e., $\tau = 0.57 \pm 0.03$ s. It is anticipated that the agreement would be improved if more configuration interaction could be considered in the calculations particularly for the evaluation of the $M2$ contribution.

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