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Excitation of inner-shell electrons by energy-pooling collisions

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We report an observation of energy-pooling collisions in a rare-earth-metal atomic element (Yb). The collisional process populates atomic states having different electronic configurations. Population transfer from closed inner-shell states to open ones is put in evidence, and its rate is comparable to the other observed collisional processes.

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I. INTRODUCTION

Since the first observation, made in 1976 by Allegrini *et al.* [1], of the energy-pooling collisions in sodium, this kind of collisional process has been widely studied in alkali-metal atoms [2]. The energy-pooling process is an effective tool to investigate atomic interactions at intermediate and long ranges and the knowledge of the cross sections allows one to test calculations on interatomic potentials. Several collisional cross sections have been measured [3–6] overcoming, by different methods, the experimental problems that this kind of measurement creates. In fact, a careful determination of excited-state densities, volumes, and lifetimes is necessary. The absolute cross sections are larger than the geometrical ones for the levels that are quasiresonant with the excited-state energy sum. The collisional process is so efficient that it can create population inversions [7] and laser emission, as it has been reported [8] on an infrared transition in sodium. More recently, the energy-pooling process has been observed in different atomic elements, that is, in Sr [9], Mg [10], Zn [11], and In [12]. In the elements of the IIA and IIB atomic groups, the energy-pooling process involves metastable levels as well as singlet-triplet levels and a weaker dependence of the cross section on the energy defect of the reaction has been found in Sr [9] as compared with the alkali-metal atoms. Also elements of group III are very interesting because collisions can excite double configuration states, some of which are also autoionizing states [12]. For Ga, In, and Tl another reaction, ionization through an energy-pooling collision, is energetically accessible and it has been observed.

In this paper we report an observation of the energy-pooling process in a rare-earth-metal element, ytterbium. This atomic element has the $4f^{14}6s^2(^1S_0)$ ground-state electronic configuration; the electrons of the closed f shell are not bound strongly, so they can be directly excited with photon energies in the near-uv optical range. This is very interesting because it gives the possibility of studying collisions involving inner-shell levels by laser spectroscopy, while for the largest part of the atomic elements more complex sources like synchrotron radiation are necessary. Beside the use of a bright laser source, the observation of collisional processes in Yb is favored by the metastability of the excited $^3P_1$ level that has a quite long lifetime equal to 875 ns [13]. This means that the transition can be easily saturated in the case of pure natural width; also in the case of a Doppler broadened transition, whose width is equal to about 500 MHz at $T=720$ K for Yb, the saturation intensity is of the order of 100 mW/cm^2, which is an easily achievable laser power density. Under a saturation regime and by taking into account the level degeneration, $\frac{3}{4}$ of the atoms are excited to the $^3P_1$ level and the excited-state collisions are enhanced.

II. EXPERIMENT

The collisional processes are studied through the analysis of the fluorescence spectra. Therefore the experiment has a standard laser-induced fluorescence (LIF) setup. Ytterbium, of natural isotopic composition, is evaporated in a cross-shaped heat-pipe oven containing 40 torr of He as a buffer gas. The use of a sealed Pyrex or quartz cell has proven to be troublesome because Yb is chemically aggressive and it rapidly darkens the glass. The temperature is controlled and regulated around 720 K, corresponding to an atomic density of the order of 10^{13} cm^{-3}; this was estimated by measuring the laser absorption over the heat-pipe effective optical length ($l=10$ cm). A cw ring dye laser pumped by an Ar^+ laser has been used to excite Yb atoms. The dye laser, operating with rhodamine 560, is tuned to the $^1S_0 \rightarrow {}^3P_1$ intercombination line at 5556 Å. The dye laser, whose power density is about 10 W/cm^2, is passively stabilized and its mode operation is controlled by a spectrum analyzer. The resonance fluorescence shows an almost complete saturation at this power density as discussed above. The single-mode laser excites either the odd isotopes of ytterbium ($m=171$, 173), having nuclear angular momentum $I\neq 0$, or all of the more abundant even isotopes ($m=172$, 174, 176; $I=0$) that cannot be resolved because of Doppler and collisional broadening. We will show in the following section that the isotopic structure of the line can be used to test the collisional processes.

The fluorescence is collected at a right angle and focused into an optical fiber. The fiber end is connected to a 1-m monochromator and light is detected by a photomultiplier. Phase-sensitive detection is used and data are stored in a computer by an acquisition system.

III. RESULTS AND DISCUSSION

A partial energy-level scheme of Yb atom is shown in Fig. 1 where the levels up to about 40000 cm^{-1} are reported in accordance with the classification of Meggers and Tech [14]. The energy E_r corresponding to twice that of the laser photons ($E_r = 2h\nu$) is represented by the dashed line. The levels are separated in columns to better indicate the allowed electric dipole transitions that follow the rigorous selection rules even↔odd parity (as well as $\Delta j = 0, \pm 1$). Different columns have also been used for levels that belong to the $4f^{14}nln'l'$ electronic configuration and for those having an excited inner shell ($4f^{13}nln'l'n''l''$); these last levels are indicated with the partial electronic configuration rather than with $(J_l j)$ designation.

As it is evident from the energy scheme, the levels with the $4f^{13}6s^2 6p_{3/2}$ electronic configuration, i.e., with an excited inner-shell electron, have an energy very close to E_r. Therefore, the energy-pooling reaction

$$\mathrm{Yb}(^3P_1) + \mathrm{Yb}(^3P_1) \rightarrow \mathrm{Yb}(4f^{13}6s^2 6p_{3/2})_j + \mathrm{Yb}(^1S_0) + \Delta E_j \qquad (1)$$

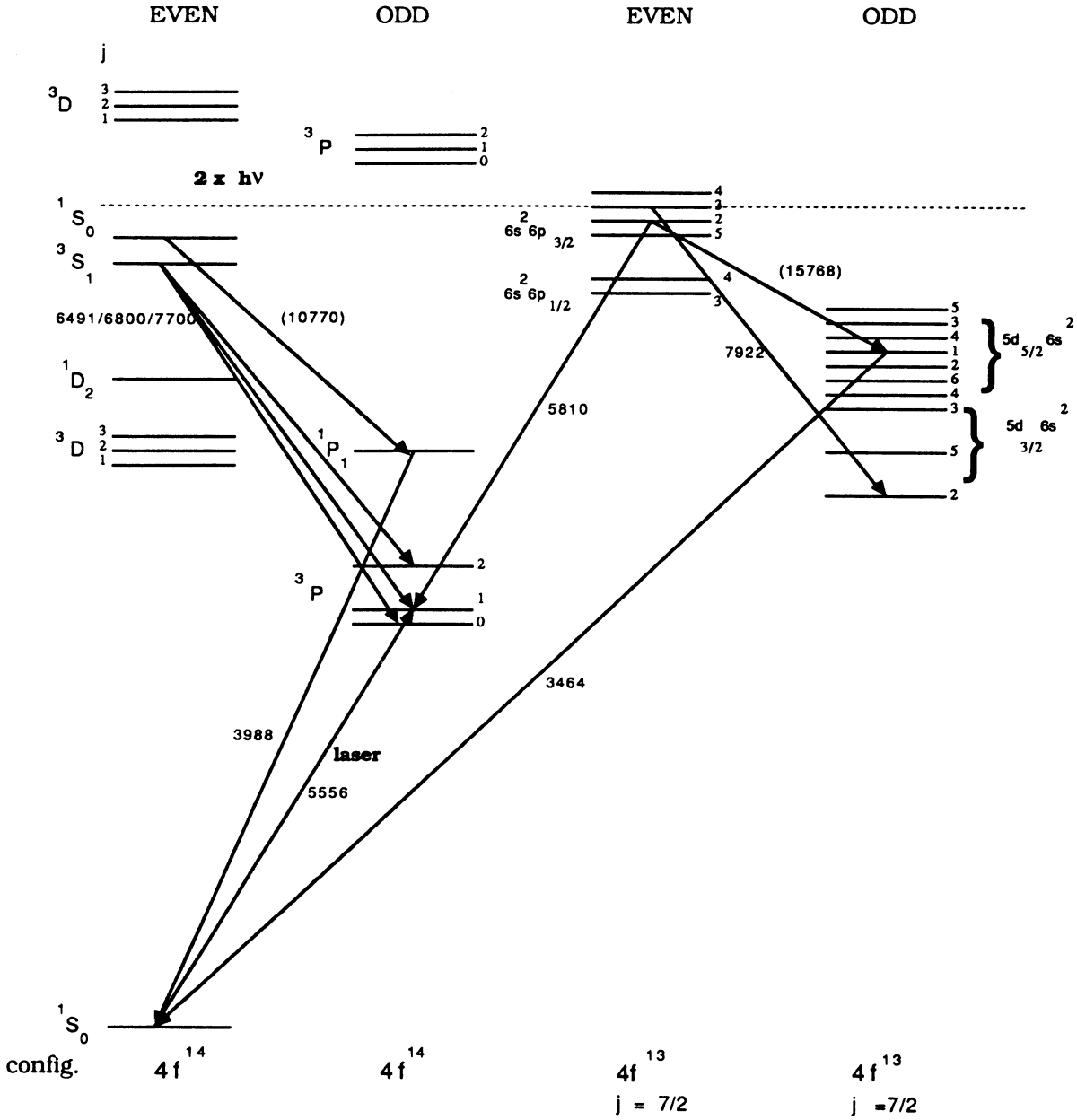

FIG. 1. Energy-level scheme of Yb with the strongest fluorescence lines indicated (in angstroms). Classification is made according to the text.

was expected to be observed in particular for $j=3$ and 2 states that have an energy defect ΔE equal to $+177$ and $+787$ cm^{-1}, respectively. These energy defects have to be compared with $kT=500$ cm^{-1} for $T=720$ K (k is the Boltzmann constant). At this temperature, two transitions coming from these levels are effectively present in the fluorescence spectrum shown in Fig. 2(a). These lines together with the strongest observed fluorescence lines are indicated in Fig. 1. In fact, beside the two transitions coming from the $(4f^{13}6s^26p_{3/2})_{j=2,3}$ levels, fluorescence lines coming from the $^3S_1$, $^1P_1$, and $(5d6s^2)_{j=1}$ states are also visible in the spectrum. The $^3S_1$ state can be populated through the energy-pooling collision

$$\mathrm{Yb}(^3P_1)+\mathrm{Yb}(^3P_1)\rightarrow \mathrm{Yb}(^3S_1)+\mathrm{Yb}(^1S_0)+\Delta E\ , \qquad (2)$$

where $\Delta E=+3290$ cm^{-1}, corresponding to $\Delta E/kT=6.6$. This energy defect, although positive, is too large to give a high collisional rate, therefore we propose another mechanism. The presence of the buffer gas makes probable a complete thermalization of the $^3P_1$ state through the

$$\mathrm{Yb}(^3P_1)+\mathrm{He}\rightarrow \mathrm{Yb}(^3P_0)+\mathrm{He}+\Delta E' \qquad (3)$$

reaction where $\Delta E'=+704$ cm^{-1} by considering that the collisional lifetime of Yb in 40 torr of He should be comparable to the optical one. For this reason the $^3S_1$ state can be populated by energy-pooling collisions of $\mathrm{Yb}(^3P_0)$ atoms with an energy defect about one-half of that associated with reaction (2). Note that in Sr for similar energy defect values the energy-pooling cross sections that resulted were quite large [9].

The other lines involving the $^1P_1$ and $(5d6s^2)_{j=1}$ states are due to radiative cascade from $^1S_0$ and $(6s^26p_{3/2})_{j=2}$ states, respectively. These radiative cascade transitions are in the infrared region, and therefore are outside our apparatus detection range. They are indicated between parentheses in Fig. 1.

The transitions discussed up to now, with the exception of those from $(4f^{13}6s^26p_{3/2})_{j=2,3}$ levels, have relatively high oscillator strengths [15,16]. On the contrary, the two optical transitions coming from the $(4f^{13}6s^26p_{3/2})_{j=2,3}$ states, whose oscillator strengths to our knowledge have not been measured yet, are indicated as very weak by Meggers and Tech [14]. In particular, the transition from $4f^{13}(6s^26p_{3/2})_{j=2}$ to $^3P_1$, which has a $4f^{14}6s6p$ configuration, should be forbidden. It exists [17] because of the configuration interaction $4f^{13}6s^26p+4f^{13}5d6s6p$. In Table I we report the intensities of the fluorescence lines at $T=720$ K, corrected for the apparatus wavelength sensitivity; they are normalized to the most intense line $^1P_1\rightarrow{}^1S_0$.

At higher temperature [$T=750$ K, Fig. 2(b)], also the transition lines from the ^3D levels are visible. These levels are endothermal for energy-pooling collisions, having negative-energy defects, but have transitions with high os-

TABLE I. Relative line intensities corrected for the apparatus sensitivity.

Transition	λ (Å)	Line intensity
$(5d6s^2)_{j=1}\rightarrow{}^1S_0$	3464.4	6.5×10^{-2}
$^1P_1\rightarrow{}^1S_0$	3988.0	1
$(6s^26p_{3/2})_{j=2}\rightarrow{}^3P_1$	5810.7	3.0×10^{-2}
$^3S_1\rightarrow{}^3P_0$	6489.1	0.19
$^3S_1\rightarrow{}^3P_1$	6799.6	0.42
$^3S_1\rightarrow{}^3P_2$	7699.5	0.77
$(6s^26p_{3/2})_{j=3}\rightarrow(5d6s^2)_{j=2}$	7922.4	8.4×10^{-2}

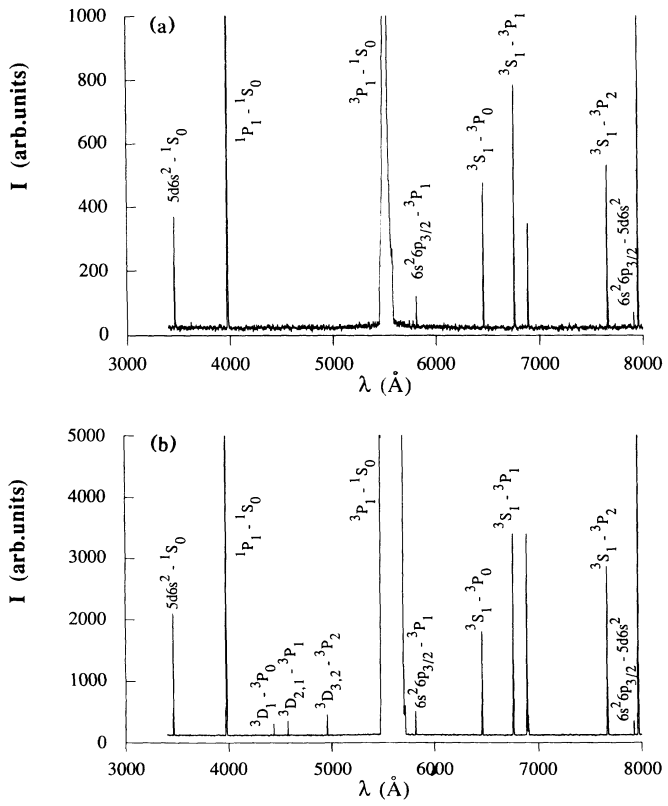

FIG. 2. Spectra of Yb after $^1S_0\rightarrow{}^3P_1$ laser excitation at two different temperatures: (a) $T=720$ K; (b) $T=750$ K. Unclassified transitions are due to second-order transmission of the monochromator.

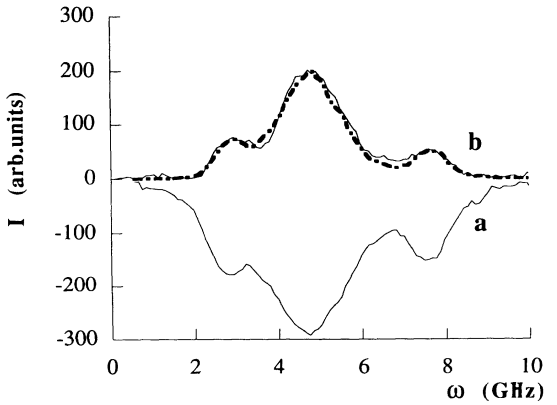

FIG. 3. Laser absorption profile a and $^1P_1\rightarrow{}^1S_0$ fluorescence line profile b as a function of the laser frequency. The dashed line represents the square of the absorption profile.

cillator strengths [16].

Our conclusions on energy-pooling collisions are supported by the dependence of the observed transition lines on different parameters. The behavior of all fluorescence lines, excluding that from the laser excited level, is similar and depends approximately on the square of the laser intensity, as the energy-pooling process forecasts. Another proof is given by the frequency dependence of the lines. In Fig. 3 we show the fluroescence intensity of the $^1P_1 \rightarrow {}^1S_0$ line and the laser absorption profile as a function of the laser frequency scanned over 10 GHz. The peak at lower frequency mainly corresponds to the excitation of the odd ^{173}Yb isotope, the central peak to the even isotopes ($m = 172$, 174, 176), and the peak at higher frequency to the ^{171}Yb and ^{173}Yb isotopes [18]. The monochromator resolution is low enough to detect the fluorescence emitted by all the isotopes in order to see the line profile due to the absorption. The reported fluroescence line profile is exactly coincident with the normalized square of the absorption profile as expected from a level populated by the energy-pooling process (or by radiative cascade from a collisionally populated level as in this case) after the reasonable hypothesis that the collisional cross section does not depend strongly on the excited isotope.

We can conclude that the reported data, even if qualitative, clearly show the occurrence of the energy-pooling process in ytterbium vapor. This collisional process seems to be very effective also in exciting inner-shell f electrons. While the measurement of absolute cross sections looks quite troublesome in a heat-pipe oven experiment, it will be possible to give the relative cross sections for different levels once the transition probabilities for all the observed states are known.

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