PHYSICAL REVIEW A VOLUME 41, NUMBER 9 1 MAY 1990

Energy-pooling ionization via an autoionizing state in indium

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(Received 10 November 1989)

Energy-transfer collisions between two $6\,^2S_{1/2}$ laser-excited indium atoms leading either to ionization of one of the colliding atoms or to population of its $n\,^2P$ Rydberg states, have been studied. Atomic lines corresponding to the $5s5p\,^2\,^2D \rightarrow 5s^2 6p\,^2P_{1/2,3/2}$ interconfiguration transitions have been recorded as evidence of the energy-pooling ionization via an autoionizing state. Atomic lines corresponding to the $n\,^2P \rightarrow 6\,^2S$ transitions for $n=9$, 10, and 11 as well as to the $5\,^2D \rightarrow 5\,^2P$ transitions have proven that the population of highly excited indium atomic states is through the energy-pooling collisions.

I. INTRODUCTION

Resonant laser excitation gives a powerful tool to atomic or molecular interaction investigations. The measured collision rates provide information on the interatomic potentials in the middle- to long-distance range, which is difficult to reach by means of other spectroscopic techniques.

In this paper we show that collisions of laser-excited atoms may be useful in the study of the interaction between different electronic configurations. The indium atom has been chosen for this purpose.

The atoms of the group-IIIa elements have the ns^2np configuration resulting in the $n\,^2P_{1/2,3/2}$ ground state. The first excited state is the $(n+1)\,^2S_{1/2}$. For all elements of this group, the energy of the first excited state is larger than half of the ionization energy (Table I). Then, the collision between two $(n+1)\,^2S_{1/2}$ excited atoms may directly lead to ionization of one of the two colliding atoms. In the case of In and Tl, due to the relatively large fine-structure splitting of their ground states, two energy-transfer processes are possible:

$$A^*+A^* \rightarrow A^+ + A_{1/2} + e^- \pm \Delta E_1 , \quad (1)$$

$$A^*+A^* \rightarrow A^{**} + A_{3/2} \pm \Delta E_2 , \quad (2)$$

where A denotes an In or Tl atom, A^* is an excited atom, A^{**} is a highly excited atom, A^+ is an A II ground state, and $A_{1/2}$ and $A_{3/2}$ denote A I ground state atoms with J equal to $\frac{1}{2}$ and $\frac{3}{2}$, respectively. The ΔE values result from the energy-conservation rule and in both cases can be accounted for by the change in the total kinetic energy of the particles.

The first process is called energy-pooling ionization (EPI),[1] because in this case the ionization energy for one of the atoms is obtained by summing up (pooling) the internal energies of both of them. The second process is the energy-pooling collision (EPC) and it has been extensively studied for alkali-metal atoms colliding in their first excited $n\,^2P$ states (e.g., see Refs. 2–5). Quite recently the EPC processes were also studied in Sr (Refs. 6 and 7) and Cd vapors.[8]

The aim of the experiment presented in this paper was to study both (1) and (2) energy transfer processes in collisions between two $\mathrm{In}(6\,^2S_{1/2})$ excited atoms. The very preliminary results were obtained in a cell containing indium and a few Torr of a buffer gas, under illumination with resonant light at a wavelength of 410.3 nm, emitted by a homemade pulsed dye laser pumped by a commercial nitrogen laser.[1] This laser has been replaced by a more powerful Nd:YAG laser (YAG denotes yttrium aluminum garnet). A detailed analysis of processes (1) and (2) can be carried out by means of spectroscopic and ionic detection. In this experiment, because of the presently un-

TABLE I. Spectroscopic data of elements of the group IIIa. The ground state of each atom is $ns^2np\,^2P_{1/2}$.

Element	Fine-structure splitting of the ground state (cm^{-1})	Energy of $(n+1)\,^2S_{1/2}$ (cm^{-1})	Energy of ionization (cm^{-1})	λ of $n\,^2P_{1/2} \rightarrow (n+1)\,^2S_{1/2}$ (nm)
B	15.2	40039.6	66928.1	249.7
Al	112.0	25347.7	48278.4	394.4
Ga	826.2	24788.6	48391.3	403.4
In	2212.6	24372.9	46670.0	410.3
Tl	7792.7	26477.5	49264.2	377.7

resolved technological difficulties, only a spectroscopic analysis has been performed.

To have a better understanding of the obtained results, it is useful to give a little information about the In level structure. The partial energy-level diagram, drawn mainly after Ref. 9, is shown in Fig. 1. Besides the $5s^25p$ configuration, the $5s5p^2$ configuration, which gives the ^4P, ^2S, ^2P, and ^2D terms, is reported. The ^2S and ^2P states lie well above (more than 10000 cm^{-1}) the ionization limit[10,11] and the three fine-structure states of the $5s5p^2\,^4P$ term are placed between the 6^2P and 7^2P terms.[9] The $5s5p^2\,^2D$ term lies about 2700 cm^{-1} above the ionization limit[12] and it is almost resonant for process (1). In the indium atomic spectrum, as in the spectra of the other atoms of group IIIa, some configuration mixing effects have already been observed.[10-13]

II. EXPERIMENTAL SETUP

We performed a cell experiment with standard apparatus. In order to have a detectable signal of energy-pooling collisions, the density of In vapor must be of the order of 10^{14} cm^{-3}. This is reached at the temperature of 1200 K. At that temperature indium becomes chemically very aggressive and even in a heat-pipe oven it needs special treatment.[14,15] To overcome these difficulties we used quartz cells. Unfortunately, after a few hours in an oven at high temperature, quartz becomes contaminated by indium and gives rise to a fluorescence background which seriously limits the effective sensitivity of the detection by making a quantitative analysis difficult.

To excite indium atoms to the $6\,^2S_{1/2}$ state we used a homemade dye laser pumped with the third harmonic ($\lambda = 355$ nm; $E = 15$ mJ per pulse) of a Nd:YAG laser (Quantel YG 585) at a repetition rate of 10 Hz. The dye employed for laser output at this wavelength is DPS (trans-4,4'-diphenylstylbene) solved in a 1,4-dioxan. The dye laser has a grazing grating configuration and it gives pulses with a length of about 15 ns and 10-kW peak power at 410.3 nm.

The fluorescence was analyzed by a 32-cm focal length monochromator (Jobin-Yvon) and detected by a photomultiplier whose output was processed by a boxcar amplifier (Stanford Research System SR 250). Due to the spectral responses of the monochromator and photomultiplier, the spectral window was in the 300–700-nm range.

In order to compare the laser-induced fluorescence spectrum with an ordinary indium atomic spectrum, we used a rf excited electrodeless lamp containing indium and a few Torr of neon.

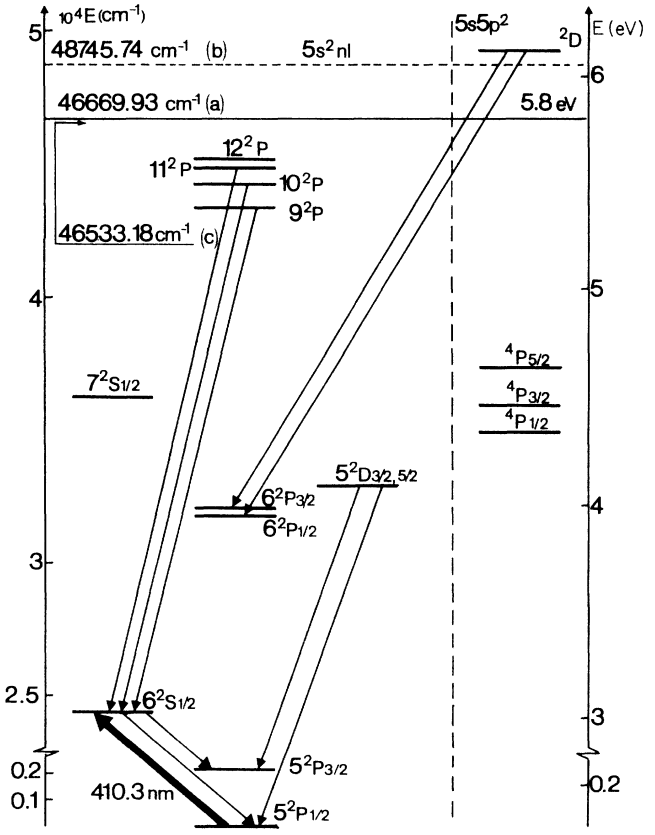

FIG. 1. Simplified indium energy-level diagram. Value (a) denotes the energy of ionization. Value (b) is twice the energy of the $6\,^2S$ state and (c) is the latter minus the $5P_{1/2}-5P_{3/2}$ fine-structure splitting. Solid lines show transitions observed under 410.3-nm laser excitation.

III. RESULTS AND DISCUSSION

The fluorescence spectra at various temperatures have been recorded under the 410.3-nm laser excitation. For relatively low temperatures the spectrum shows only two atomic lines corresponding to the $6\,^2S_{1/2} \rightarrow 5\,^2P_{1/2,3/2}$ transitions. Their ratio changes, by increasing the vapor density, due to the radiation trapping effect, and the $6\,^2S_{1/2} \rightarrow 5\,^2P_{3/2}$ transition line becomes more intense than the other one. When the density of indium vapor is high enough, the $9\,^2P, 10\,^2P, 11\,^2P \rightarrow 6\,^2S$ as well as the $5\,^2D \rightarrow 5\,^2P_{1/2,3/2}$ lines also appear. Their intensities are 5–6 orders of magnitude lower than the fundamental ones. The presence in the spectrum of these atomic lines is ascribed to the process

$$\mathrm{In}(6\,^2S_{1/2}) + \mathrm{In}(6\,^2S_{1/2}) \rightarrow \mathrm{In}(5\,^2P_{3/2}) + \mathrm{In}(n\,^2P_{1/2,3/2}) + \Delta E\,, \qquad (3)$$

which is within 3 cm^{-1} of resonance with the $32\,^2P$ state.[15] Due to the limited spectral response of our apparatus, we could not detect any transitions from $n\,^2P$ to the $5\,^2D$ state, but we suppose that the latter is populated by these cascade transitions. The lines corresponding to the $5\,^2D \rightarrow 5\,^2P_{1/2,3/2}$ transitions, as well as all other lines, disappear whenever the exciting light is out of resonance.

In process (3), according to the general selection rule that $S \rightarrow S$ as well as $S \rightarrow D$ transitions are forbidden, we could expect only the population of $n\,^2P$ states. This selection rule is not strictly obeyed,[16] but in our case the intensities of the other possible lines would be too weak to be recorded.

The ionization energies E_i and the values of the corresponding ΔE for some $n\,^2P$ states are given in Table II.

We suppose that in the case of $11\,^2P$, $10\,^2P$, and $9\,^2P$ levels populated by the energy-pooling collisions, the radiative transition rates to the $6\,^2S$ level are larger than the cross section for those secondary collisional processes which would lead to ionization from each of these upper states.

At the temperature of 1223 K and under resonant laser excitation, the intensities of the recorded lines originating from $n\,^2P$ states with $n=11$, 10, and 9 are in the ratio 3:1:1. We did not observe the line corresponding to the $12\,^2P\rightarrow 6\,^2S$ transition as well as any other line originating from $n\,^2P$ states with n larger than 12, even though the corresponding energy defects ΔE (Table II) are more favorable. This peculiar line intensity behavior may be compared with other indium spectra obtained under various excitations or in absorption.

In the $n\,^2P\rightarrow 6\,^2S$ series of the rf excited electrodeless indium lamp spectrum, transitions from states with $n=12$, 11, and 10 are absent. The line at 468.2 nm, corresponding to the $14\,^2P\rightarrow 6\,^2S$ transition, is anomalously strong and the intensities of the other lines of this series are in the ratio 8:1:7 for $n=8$, 9, and 13, respectively.

These anomalies of line intensities are confirmed in other papers which, unfortunately, are not so numerous, probably due to the difficulties of working with indium (i.e., the rather low vapor pressure and strong alloying tendency[14]). In earlier works the absorption spectra in the near and vacuum ultraviolet were observed.[10–12,17] More recently the atomic spectrum was studied by means of two-photon excitation coupled with ion detection.[13,15] Information about intensities of the observed atomic transitions are given in some of the cited papers. For example, in the $5\,^2P_{3/2}\rightarrow n\,^2D$ series the $5\,^2P_{3/2}\rightarrow 10\,^2D_{3/2}$ absorption line is absent and in the $5\,^2P_{1/2}\rightarrow n\,^2D_{3/2}$ series the lines for $n=8$ and 9 are considerably weaker than the lines for $n=10$ and 11.[11] In the experiment with two-photon excitation followed by collisional ionization, the $7\,^2F$ and $10\,^2P$ level populations were not observed due to the very low signal intensities, and in the case of the $6\,^2F$ and $9\,^2P$ levels the signal was anomalously weak. On the other hand, the photoionization signal due to population of the $11\,^2P$ was quite intense.[14] Moreover, in an experiment on the indium level isotope shift, the transition to the $10\,^2F_{5/2}$ level is missing in the two-photon excited series $5\,^2P_{1/2}\rightarrow n\,^2F_{5/2}$.[15]

In general, a likely explanation of these intensity peculiarities is given by the theory of line shapes and intensity distributions concerning resonances between discrete states and autoionizing states lying in the continuum.[18–20] The perturbations in intensity of the indium atomic lines are due to the presence of the $5s5p^2\,^2D$ autoionizing state. However, it is evident that in the case of the $6\,^2S_{1/2}$ resonant laser excitation, the $n\,^2P$ Rydberg-state populations (observed through the recorded lines intensities) have a different behavior than the one observed in the rf excited electrodeless lamp. This strongly supports the presence of a different population mechanism, which is the energy-pooling collision.

The energy-pooling ionization in collision between two excited indium atoms, which is competitive with process (3), is described by the reactions

$$\mathrm{In}(6\,^2S_{1/2})+\mathrm{In}(6\,^2S_{1/2})\rightarrow \mathrm{In}(5\,^2P_{1/2})+\mathrm{In}^+ + e^- + \Delta E(2075.8\ \mathrm{cm}^{-1}), \quad (4a)$$

$$\mathrm{In}(6\,^2S_{1/2})+\mathrm{In}(6\,^2S_{1/2})\rightarrow \mathrm{In}(5\,^2P_{1/2})+\mathrm{In}(5s5p^2\,^2D) - \Delta E(554\ \mathrm{cm}^{-1}). \quad (4b)$$

Process (4a) leads to the ordinary ionization of an indium atom. Process (4b) is within kT of resonance with the $5s5p^2\,^2D$ autoionizing state and it can be followed by autoionization, in which case it appears similar to process (4a). Following ionization by either mechanism, radiative recombination may lead to population of one of the discrete states belonging to the $5s^2nl$ configuration.

We have not performed any electronic or ionic detection. Nevertheless we have direct evidence of process (4b). In fact, in the fluorescence spectrum, the lines at wavelengths of 572 and 582 nm, corresponding to the $5s5p^2\,^2D\rightarrow 5s^2 6p\,^2P_{1/2,3/2}$ transitions, appear when the laser is on resonance and the vapor density is high enough to observe the other lines due to process (3). The intensity ratio for lines corresponding to the $11\,^2P\rightarrow 6\,^2S$ and $5s5p^2\,^2D\rightarrow 5s^2 6p\,^2P_{1/2,3/2}$ transitions is 2:1. Because of the limited resolution of our apparatus we could only estimate the position of the autoionizing state as 49 300 cm^{-1}, which is 2630 cm^{-1} above the ionization limit. In the indium lamp spectrum we did not observe any lines corresponding to these transitions. This confirms that the ^2D autoionizing state is efficiently populated in process (4b).

In this experiment we could not measure an ionization current, so we have no direct evidence of process (4a). However, we can estimate from the results obtained by Mirza and Duley[13] how efficient the process is. They recorded an enormous photoionization signal when the $5\,^2P_{3/2}\rightarrow 6\,^2S_{1/2}$ transition was excited by resonant light at a wavelength of 451.26 nm. This two-photon excitation experiment was performed in a cell containing indium vapor and 20 Torr of helium, heated to the temperature of 1270 K, which corresponds to an indium atom concentration of $3.6\times 10^{14}\ \mathrm{cm}^{-3}$. The result was interpreted as due to a hybrid resonance. In our opinion, processes (4a) and (4b) are responsible for the large photoionization signal, especially when one takes into consideration the rather low concentration of indium molecules in the vapor.

TABLE II. Data of $n\,^2P_{3/2}$ states involved in process (3).

n	Level energy E (cm^{-1})	Energy of ionization E_i (cm^{-1})	ΔE (cm^{-1})	$n\,^2P\rightarrow 6\,^2S$ λ (nm)
8	41 881.4[a]	4788.5	4651.8	571.1
9	43 399.5[a]	3270.4	3133.7	525.6
10	44 294.1[a]	2375.8	2239.1	502.0
11	44 865.8[a]	1804.1	1667.4	488.0
12	45 252.3[b]	1417.6	1280.9	478.9
13	45 527.8[b]	1142.1	1005.4	472.7

[a]Reference 9. [b]Reference 13.

IV. CONCLUSIONS

An autoionizing state has been populated by energy-pooling collisions and the interconfiguration transitions in the fluorescence spectrum have been recorded.

We have also observed a few atomic lines originating from states populated in process (3), which confirm that in the case of indium, energy-pooling collisions leading to the population of high-lying levels are also possible.

ACKNOWLEDGMENTS

One of us (A.K.) wants to express heartfelt thanks to the director and to the staff of Instituto di Fisica Atomica e Molecolare, Consiglio Nazionale delle Ricerche (CNR) in Pisa. This research has been supported by Gruppo Nazionale Struttura della Materia of CNR and in part by the Polish Ministry of National Education (research Project No. CPBP 01.06).

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