

Inverted fine structure in highly excited 2F Rydberg states of indium

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Fine structure in the 2F Rydberg states of indium has been studied by optical-microwave double-resonance spectroscopy. Microwave transitions between the neighboring levels of the ${}^2F_{5/2}$ and ${}^2F_{7/2}$ Rydberg series have been measured for the range of $n=35, 36,$ and $39-41$. The experimental results show that the fine structure of the 2F states is inverted. The observed inversion in the fine structure is found to be closely correlated with a long-range interaction between the inner core and the valence electron of the atom.

I. INTRODUCTION

The physical properties of highly excited Rydberg atoms, such as the energy-level structure and the lifetimes of Rydberg states, have been studied in a number of laboratories since the end of the 1970's [1-3]. However, most of these studies have been limited to the Rydberg states of alkali-metal and alkaline-earth atoms. Furthermore, there are very few studies on the high-lying states with large orbital angular momentum. The extension of the study to non-alkali-metal and non-alkaline-earth atoms is of particular interest for the development of the theoretical modeling because of their complex electronic configuration.

The motivation of the study of energy-level structures in nonhydrogenic atoms comes from an interest in the deviation from hydrogenic theory. In atomic fine structure, such deviations appear as anomalously large or small fine-structure splittings, sometimes even an inversion of level ordering. The study of the fine structure of alkali-metal Rydberg states by laser spectroscopy has revealed that anomalous fine-structure splittings appear also for highly excited states despite their quasihydrogenic character. For Na and K, the fine structure was observed to be inverted for the $nd\ {}^2D$ states [4-10], whereas the $nf\ {}^2F$ states were reported to have inverted structures for Rb and Cs [11-14].

In the present work, we studied the fine structure in the high Rydberg states of the 2F series of indium. The ground state of the indium atom has the $5s^25p$ configuration with three electrons outside the closed shells. As the two s electrons form a closed subshell, the residual electron gives rise to an alkalilike spectrum. The $ns\ {}^2S_{1/2}$, $np\ {}^2P_{1/2,3/2}$, and $nd\ {}^2D_{3/2,5/2}$ Rydberg series of indium have been studied by Dönszelmann and his co-workers using one-photon, two-phonon, and stepwise laser excitation [15-18]. In their studies, the fine-structure splittings of the $np\ {}^2P$ and $nd\ {}^2D$ levels were

found to be normal. Although the $nf\ {}^2F$ Rydberg series has been studied for the lower n states [19-21], there are no reliable experimental data for the fine structure. In Moore's table [19], the fine structure is normal for $n=4$ and 7 , inverted for $n=8-10$, and again normal for $n=11$. On the other hand, Johansson and Litzén reported that the fine structure for $n=4$ and 5 can be inverted by about 0.02 cm^{-1} [20]. Recently, we have observed the $nf\ {}^2F$ Rydberg series ($n=30-79$) by two-color laser ionization spectroscopy [22,23]. The analysis of the optical spectrum suggested that the fine structure of 2F states is inverted with very small splitting.

In the present paper, we report an observation of the fine structure in the $nf\ {}^2F$ Rydberg series of indium by optical-microwave double-resonance spectroscopy. The direct measurement of the energy differences between the high-lying Rydberg states with a linewidth of less than 1 MHz is easily achieved owing to the long lifetime of high Rydberg states.

II. EXPERIMENTAL SETUP

The experimental setup is similar to the one used previously for the investigation on the Rydberg states in ytterbium and lutetium [24,25]. A schematic diagram of the setup is shown by Fig. 1. Highly excited Rydberg states of indium were prepared by irradiation of two pulsed dye-laser beams (one frequency doubled by a BBO crystal) onto a collimated atomic beam generated by a resistively heated oven.

We used the excitation scheme shown in Fig. 2 to populate the $nf\ {}^2F_{5/2,7/2}$ states. The $nf\ {}^2F_{5/2}$ Rydberg states were excited from the ground state $5p\ {}^2P_{1/2}$ via the intermediate state $5d\ {}^2D_{3/2}$, while the $nf\ {}^2F_{7/2}$ Rydberg states were excited from a thermally populated metastable state $5p\ {}^2P_{3/2}$ via the intermediate state $5d\ {}^2D_{5/2}$. The two-photon microwave transitions between the Rydberg states were induced by continuous microwave radiation from several millimeter-wave klystrons, which covered the frequency ranges of 30-56 and 62-78 GHz. The transition frequency was calibrated with a frequency marker that was produced by mixing the millimeter wave and higher harmonics of an X-band Gunn oscillator, the

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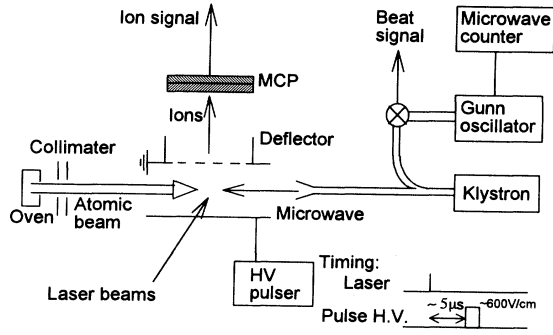


FIG. 1. Schematic diagram of the experimental setup for the optical-microwave double-resonance spectroscopy.

frequency of which was measured directly with a microwave frequency counter.

Resonant microwave transitions were detected by the selective field-ionization method [26]. After a few microseconds from the laser pulse, a pulsed electric field of appropriate strength (maximum 600 V/cm) was applied in order to ionize the atoms in the upper state of the microwave transition selectively. The ions produced were then accelerated toward a microchannel plate (MCP) through a grid prepared in the middle of the upper electrode.

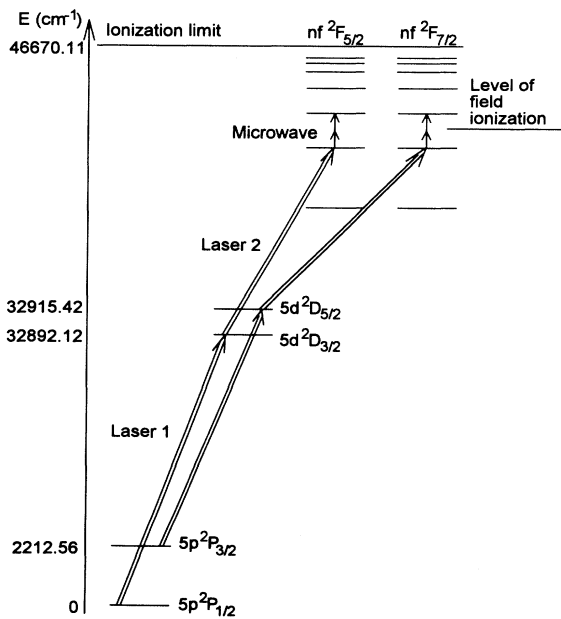


FIG. 2. Excitation scheme of the indium atom for the highly excited 2F Rydberg states. The double and single lines with arrows indicate the two-step optical excitation and the microwave transitions, respectively.

III. RESULTS AND ANALYSIS

We measured the transition between the neighboring Rydberg states by optical-microwave double-resonance spectroscopy to determine the fine structure of the highly excited Rydberg states. The $(n+1)f^2F_J \leftarrow n f^2F_J$ ($J = \frac{5}{2}, \frac{7}{2}$) two-photon microwave transitions were observed for $n = 35, 36,$ and $39-41$. This assignment was based on the transition frequencies calculated using the quantum defects given in Refs. [22] and [23]. All the measured frequencies are given in the third column of Table I. The range of the measurable principal quantum number n is limited by the frequency range covered by the millimeter-wave klystrons in our laboratory, and also by the resolution of the selective field ionization when n is increased.

Figure 3 shows a trace of the microwave transition $36f^2F_{7/2} \leftarrow 35f^2F_{7/2}$. Resolution of the microwave transition, usually in the order of MHz (full width at half maximum) has been limited mostly by the frequency instability of the klystron. The intervals in the 2F fine structure could not be directly measured in the present two-photon microwave transition because the transition probability of the two-photon process $(n+1)^2F_{5/2} \leftarrow n f^2F_{7/2}$ or $(n+1)f^2F_{7/2} \leftarrow n f^2F_{5/2}$ is considerably smaller than those of the $\Delta J = 0$ transitions.

The level ordering of the components of the doublet 2F can be derived from the comparison of the measured frequencies in the ${}^2F_{5/2}$ and ${}^2F_{7/2}$ series. As shown in Table II, each transition frequency in the ${}^2F_{5/2}$ series is smaller than that of the corresponding transition in the ${}^2F_{7/2}$ series. This means that each energy level in the ${}^2F_{5/2}$ series is located above the corresponding level in the ${}^2F_{7/2}$ series, since both the ${}^2F_{5/2}$ and the ${}^2F_{7/2}$ series converge to the same ionization limit. In an hydrogenic atom, the level with angular momentum $J = l + \frac{1}{2}$ is located above the $J = l - \frac{1}{2}$ states. Thus, the inversion of the fine structure in the 2F series of indium is obvious.

The experimental data were analyzed by a least-squares-fit to the general Rydberg-Ritz formula,

$$E_n = E_i - R / (n - \delta_n)^2, \quad (1)$$

where E_n is the energy of the Rydberg state with quan-

TABLE I. The two-photon $(n+1)f^2F_J \leftarrow n f^2F_J$ ($J = \frac{5}{2}, \frac{7}{2}$) transitions. The energy interval of this transition corresponds to twice the quoted frequencies.

Series	n	Obs. (MHz)	Calc. (MHz)	Obs. - Calc. (MHz)
${}^2F_{5/2}$	35	73 818.38	73 818.40	-0.02
	36	67 907.64	67 907.64	0.00
	39	53 563.28	53 563.21	0.07
	40	49 687.98	49 688.00	-0.02
	41	46 177.75	46 177.80	-0.05
${}^2F_{7/2}$	35	73 819.31	73 819.28	0.03
	36	67 908.33	67 908.38	-0.05
	39	53 563.65	53 563.67	-0.02
	40	49 688.46	49 688.39	0.07
	41	46 178.11	46 178.14	-0.03

TABLE II. The frequency differences between the observed microwave transitions of the ${}^2F_{5/2}$ and ${}^2F_{7/2}$ series (the frequency of the ${}^2F_{5/2}$ series minus that of the ${}^2F_{7/2}$ series).

n	Frequency difference (MHz)
35	-0.93
36	-0.69
39	-0.37
40	-0.48
41	-0.36

tum number n , E_i is the convergence limit (ionization limit) of the Rydberg series, R is the Rydberg constant for the relevant atom (for indium $R = 109\,736.7914\text{ cm}^{-1}$), and

$$\delta_n = \alpha + \beta / (n - \delta_n)^2 + \dots \quad (2)$$

is the quantum defect that is expanded in a power series of the inverse square of the effective quantum number $n^* = n - \delta_n$ to include the energy dependence of the quantum defect. For the sake of simplifying the numerical computation, we treated the quantum defect δ_n as

$$\delta_n = \alpha + \beta / (n - \alpha)^2 + \dots \quad (2')$$

The final fitting parameters are listed in Table III. Uncertainty quoted in the table is one standard deviation.

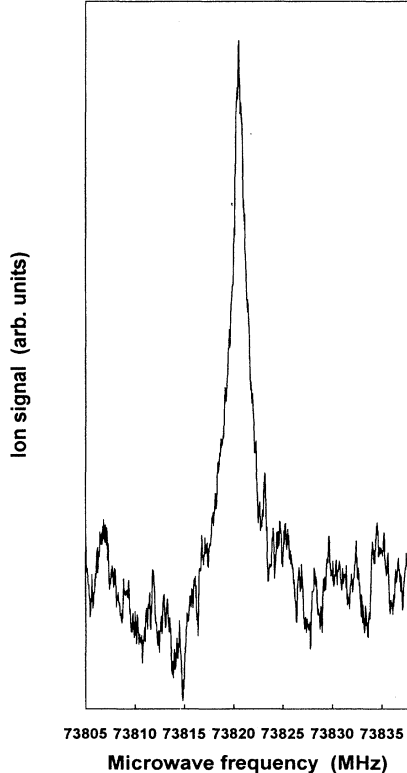


FIG. 3. The line profile for the $36f^2 F_{7/2} \leftarrow 35f^2 F_{7/2}$ two-photon microwave transition. The center of the spectrum is $73\,819.31\text{ MHz}$. The linewidth is about 1 MHz .

TABLE III. The quantum defects α and β for the ${}^2F_{5/2}$ and ${}^2F_{7/2}$ series.

Series	α	β
${}^2F_{5/2}$	0.039 98(3)	0.73(3)
${}^2F_{7/2}$	0.039 98(4)	0.84(3)

Figure 4 displays the calculated quantum defects δ_n of the ${}^2F_{5/2,7/2}$ series as a function of n , together with the literature values [15,16] of the ${}^2P_{1/2,3/2}$ and ${}^2D_{3/2,5/2}$ series. Unlike in the ${}^2P_{1/2,3/2}$ and ${}^2D_{3/2,5/2}$ series, δ_n of the $J = l + \frac{1}{2}$ states are larger than that of the $J = l - \frac{1}{2}$ states in the ${}^2F_{5/2,7/2}$ series, reflecting the inverted fine structure. It should be noted that extremely small quantum defects of the ${}^2F_{5/2,7/2}$ series are due to the “non-penetration” of the In^+ core by the valence electron. Even though the high- l Rydberg electrons do not penetrate the core, they do polarize it, and this also leads to nonzero quantum defects.

The calculated transition frequencies with an overall accuracy of 0.04 MHz (one standard deviation) are listed in the fourth column of Table I. The differences between the observed and calculated frequencies, which are less than 0.07 MHz , are listed in the fifth column. The absence of the systematic deviation between the observed

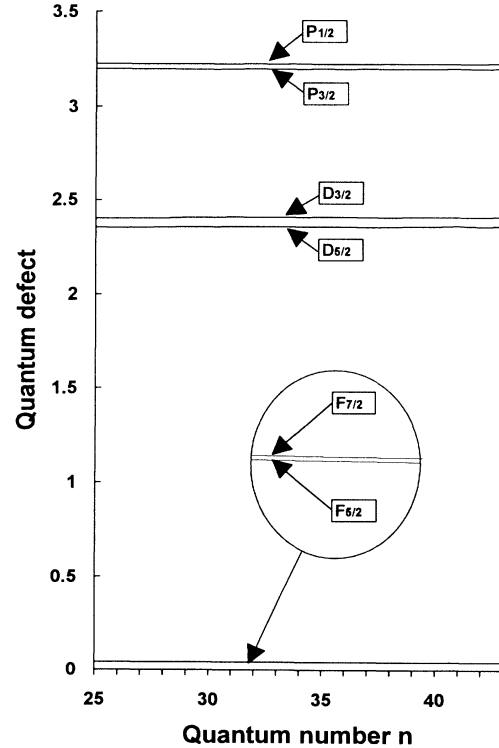


FIG. 4. Quantum defects of the ${}^2P_{1/2,3/2}$, ${}^2D_{3/2,5/2}$, and ${}^2F_{5/2,7/2}$ Rydberg series as a function of the quantum number n ; literature values [15,16] for the ${}^2P_{1/2,3/2}$ and ${}^2D_{3/2,5/2}$ levels, and present fitting values for the ${}^2F_{7/2,5/2}$ levels are given.

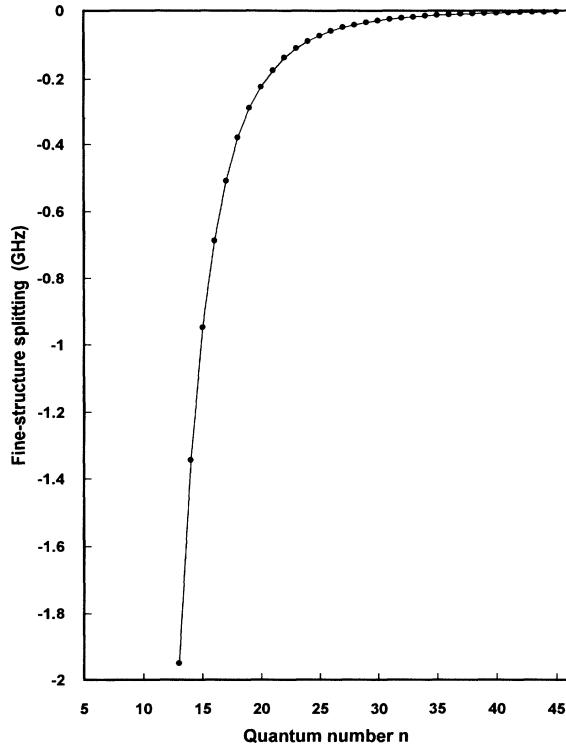


FIG. 5. The fine-structure splitting in the 2F series of In as a function of the principal quantum number n . The solid line indicates the calculated n dependence of the fine structure using the formula developed by Chang (see text).

and calculated microwave transition frequencies indicates that there is no local perturbation in the studied region.

Figure 5 plots the fine-structure splitting as a function of n using the calculated results of the quantum defects. Because our results show that all of the fine structure of the 2F states should be inverted, we consider that the splittings reported to be normal and inverted for different n in the lower n states in Moore's energy tables [19] are simply due to experimental inaccuracy.

IV. DISCUSSION

The characters of nonhydrogenic atoms are sometimes explained by the "configuration interaction," where the true electronic wave functions are regarded as mixtures of the wave functions of those states of the independent-particle model that belong to the configurations of identical parity and angular momentum [27]. For example, the inversion of the fine structure observed in alkali-metal atoms was interpreted by the configuration interaction. As stated in the Introduction, the level inversion was found in the 2D state for Na and K, whereas for Rb and Cs the level inversion was found in the 2F state. We note that for Na and K the core p electrons may easily be excited into the lowest excited d orbital, and for Rb and Cs the core d electrons may also be excited into the lowest excited f orbital. Actually, the inverted fine structure of the Na $3d$ states was reproduced by Beck and Odabasi

[28] using the $2p^63d-2p^5np3d$ configuration interaction with reasonable accuracy.

In the case of In, fine-structure splitting of the 2D series was found to be strongly affected by the perturbation from the $5s5p^2$ configuration, although there exists no level inversion in the 2D series [15,18,27]. However, it is difficult to explain the occurrence of the inversion in the 2F series using configuration interaction. One possible candidate of the perturbers for the ${}^2F_{5/2}$ series is an autoionization level $5s5p6s^4P_{5/2}^o$, which is located at $68\,821.7\text{ cm}^{-1}$. The perturbation from this level tends to lower the levels of the ${}^2F_{5/2}$ series, and as a result to increase the size of normal splitting but not to produce the inversion in the fine structure.

For elucidating the origin of the inversion in the fine structure, a numerical fitting was employed for the inverted fine structure of the 2F series. The basic formula

$$\Delta_{\text{fs}}(n,l) = N_l(n)(a + b/n^2 + c/n^4 + \dots) \quad (3)$$

was developed by Chang [29,30], where

$$N_l(n) = n^{-3} \prod_{p=0}^l [(n^2 - p^2)/n^2]. \quad (4)$$

This formula has several important advantages [30] compared to the expression

$$\Delta_{\text{fs}} = A/n^{*3} + B/n^{*5} + C/n^{*7} + \dots, \quad (5)$$

where Δ_{fs} is expanded in odd powers of n^* :

(a) If a relative magnitude of the absolute values of b and c to that of a is large, the range of the interaction (long or short) that is responsible for the doublet splitting should be considered to be long.

(b) The principal quantum number n is used instead of the effective quantum number n^* , which is determined by the measurement of the term value of a specific energy level.

(c) This fitting is free from the difficulty met in some analyses of alkali atoms with Eq. (5).

Using the fine-structure splitting of the $nf\,{}^2F$ series calculated from the quantum defects in Table III, we obtain

$$a = 18(5)\text{ GHz},$$

$$b = -7.15(3) \times 10^5\text{ GHz},$$

$$c = -1.28(3) \times 10^7\text{ GHz}.$$

The curve reproduced from these parameters is drawn as a full line in Fig. 5.

The present analysis indicates that the absolute value of parameters b and c are larger than the leading parameter a . According to the above characteristic (a), the present fitting results suggest that the long-range interaction contributes significantly to the level inversion in the 2F state of indium.

Theoretically, two types of approaches have been used to reproduce the inversion in fine structure. The first was introduced by Sternheimer and his co-workers [31] using an exchange core-polarization model, where the fine-structure interval was derived from the interaction of the valence electron with the core through the polarization of

the core electrons. The second approach, which was introduced by Luc-Koenig [32], is apparently quite different since it starts from an independent-particle (central field) relativistic model. The two methods were both successful and have been shown to have almost equivalent results [33].

The inversion in the 2F states of indium has been predicted by Pyper and Marketos [34] with an *ab initio* calculation including a first-order relativistic correction to the Hartree-Fock energy, which is the development of the approach introduced by Luc-Koenig [32]. It was found that the main origin for the anomalous fine structure is the relativistic shifts of the core orbitals, which cause the exchange potential for the valence electron to be J dependent.

The theoretical value of the fine-structure splitting by Pyper and Marketos [34] is $-9 \times 10^{-5} \text{ cm}^{-1}$ for $n=30$.

If we consider the hydrogenic fine-structure splitting for $n=30$, $1.8 \times 10^{-5} \text{ cm}^{-1}$, the net correction by their calculation is $-1.1 \times 10^{-4} \text{ cm}^{-1}$. On the other hand, the splitting calculated from our experimental data is $-9.6 \times 10^{-4} \text{ cm}^{-1}$, which makes the net correction $-9.8 \times 10^{-4} \text{ cm}^{-1}$. Thus, the theoretical value is about $\frac{1}{9}$ the experimental value. The interpretation of this discrepancy is a problem that will be left to the future.

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