Temperature-dependent depolarization cross sections of the $5d6p\ ^3P_1$ and $^3D_1$ states of laser-ablated Ba in He gas in the range 10–300 K

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We have applied the laser-ablation technique for the study of depolarization effects of the $5d6p\ ^3P_1$ and $^3D_1$ states of Ba with He gas in the wide temperature range of 10–300 K. The depolarization cross sections of both states have been found to have a positive temperature dependence, indicating that the responsible interaction is not a van der Waals type. A tentative and qualitative explanation for the difference of the temperature dependence between $5d6p\ ^3P_1$ and $^3D_1$ is given in terms of electron density distribution. [S1050-2947(98)07005-X]

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Investigation of the destruction of alignment due to collisions is one of the fundamental problems in atomic and molecular physics. The alignment of atoms or molecules is defined as an anisotropic but symmetric distribution of population among magnetic sublevels, and can be created by the use of polarized laser light or collisional excitation with certain symmetry. So far, most of the experimental study of such processes has been limited to the case with buffer gas above several hundred kelvins [1,2]. This is especially true for metal atoms whose melting points are usually as high as 1000 K or above. For such atoms, special equipment such as an atomic oven or a discharge tube is required in order to obtain a sufficient number of atoms at a gas temperature below melting point.

The use of the laser-ablation technique is one way out of the difficulty. Recently we have applied the laser-ablation technique for the study of depolarization effects of Ba $5d6p$ $J=1$ states in He gas at room temperature [3]. Obviously, it is even more difficult at a temperature as low as ~ 10 K to employ other methods for the creation of metal atoms, since the use of an atomic oven or discharge would lead to the significant increase of the buffer gas temperature. It should be noted that 300 K corresponds to the kinetic energy of 26 meV, and 10 K to 0.9 meV. It is not known yet how the collisions take place at such a low energy regime. According to the semiclassical impact parameter method [4], the depolarization cross section should have $T^{-1/(n-1)}$ dependence if the responsible interaction is represented by R^{-n}, where R is an internuclear distance between colliding atoms.

In this paper we demonstrate the feasibility of the ablation technique for the study of depolarization effects of laser-excited $5d6p\ ^3P_1$ and $^3D_1$ states of Ba with He buffer gas in the range of 10–300 K. The purpose is to investigate the temperature dependence of the depolarization cross sections in the very small collision energy regime.

Before going into details of our study, we note that there are only a few experimental studies that report the temperature dependence of depolarization effects. Belsley *et al.* [5] have studied the temperature dependence of depolarization for the Ba($6s6p\ ^1P_1$)-Ar and Ba($6s6p\ ^1P_1$)-Xe systems under off-resonance excitation in the range of 800–1200 K using a heat pipe, and concluded that the temperature dependence is rather small for Ba $6s6p\ ^1P_1$ in that temperature range. Ishitani *et al.* [6] have reported a positive temperature dependence of depolarization cross sections for the laser-excited $2p^5 3p\ J=1$ states of Ne from the metastable $2p^5 3s$ $J=0$ state produced in a dc discharge plasma in the range of 77–640 K. Bahrim *et al.* [7] have made quantal close-coupling calculations of disalignment cross sections for the Ne($2p^5 3p$)-He system, which are in good agreement with the experimental results by Wakabayashi *et al.* [8].

The level scheme we consider is shown in Fig. 1(a). The Ba atom in the ground state $6s^2\ ^1S_0$ is excited by a linearly polarized laser to the $5d6p\ ^3P_1$ or $^3D_1$ state. Defining the quantization axis along the polarization vector of the laser, only the $J=1$, $m=0$ sublevel is populated because of the selection rule of dipole transitions in terms of magnetic sublevels. Under the presence of buffer gas, however, collisional relaxation takes place as indicated by the transfer rates Γ_a and Γ_b in Fig. 1(b). The elastic population transfer given by these rates is responsible for the depolarization. The rate Γ_a can be determined from the intensity ratio of the laser-induced fluorescence (LIF) with two polarization components $I_\parallel$ and $I_\perp$ with respect to the polarization axis of the incident excitation-laser beam. The rate Γ_b remains to be undetermined in our case because of the symmetry of the system, i.e., linearly polarized light and isotropic collisions.

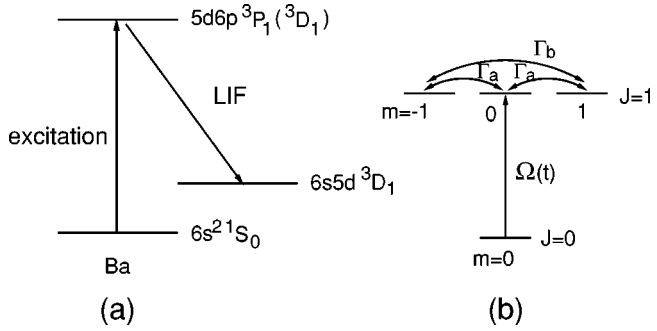

FIG. 1. Level scheme. (a) The Ba atom in the ground state is excited to the $5d6p\ ^3P_1$ ($^3D_1$) state by a linearly polarized laser. (b) Under the buffer gas environment, the collisional relaxation takes place among magnetic sublevels. Such rates are denoted by Γ_a and Γ_b. For details, see text.

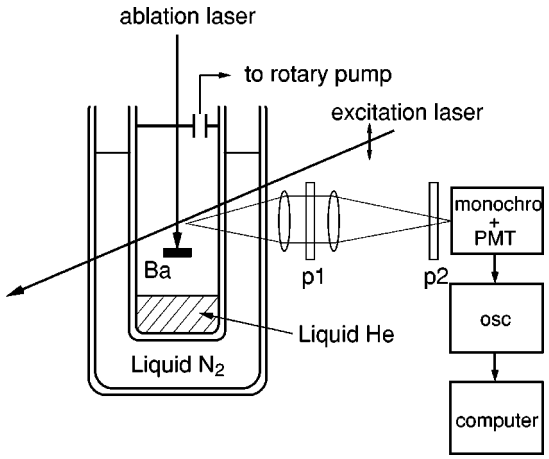

FIG. 2. Experimental setup. The polarization of the LIF is selected by the first polarizer ($p1$), while the second one ($p2$) is fixed with a polarization axis of 45° in order to ensure the equal detection sensitivity for both $I_{\parallel}$ and $I_{\perp}$.

The experiment is performed using two lasers, i.e., a Nd:YAG laser (Quanta-Ray GCR-12S, 1.06 μm or 355 nm, 10 ns pulse duration) for the ablation of a solid Ba sample and a dye laser (Lambda Physik FL3002, 18 ns pulse duration), which is pumped by a XeCl laser (Lambda Physik MSC103) for the excitation of laser-ablated Ba (see Fig. 2). The energies of the lasers used throughout the present study are $\sim$40 mJ/pulse and $\sim$20 μJ/pulse for ablation and excitation, respectively. The solid Ba sample is placed in an inner vessel of a double-bath Pyrex dewar. Each wall of the dewar has a double-layer structure with a narrow gap kept in vacuum for the thermal insulation. The ablation laser is loosely focused onto the Ba sample, and the resulting spot size and the energy density are $\phi = 1$ mm and $\sim 10^8$ W/cm^2, respectively. From the spectra of laser-induced plasma, it is found that the ablated sample consists of both neutral and ionic species of Ba. After approximately 500 μs delay, a pulsed dye laser beam, which is linearly polarized using a Glan-Thompson prism, is sent into the excitation region. The excitation region is approximately 1.5 cm above the sample. Note that the delay time of 500 μs has been introduced so that the Ba-He system reaches a thermal equilibrium before laser excitation. Later in this paper we will explain why this delay time is considered to be sufficient for the thermalization of laser-ablated Ba atoms in He gas. The temperature is read by a thermocouple placed about 2 cm off from the laser-excitation region. We have found that the use of the third harmonics of the YAG laser is particularly useful for the realization of ablation below liquid nitrogen temperature (77 K). Using a photomultiplier (Hamamatsu-Photonics R955) together with a monochromator (JASCO CT25), the LIF is observed through a pair of lenses and two polarizers. Observation direction and the polarization vector of the excitation laser are perpendicular to each other as usual. The polarization axis of the second polarizer ($p2$) is set at 45° around the optical axis of the monochromator in order to ensure that the detection efficiency does not depend on the detected polarization component $I_{\parallel}$ or $I_{\perp}$ of the LIF, which is selected by the first polarizer ($p1$). Thus the obtained LIF signal is further sent to a preamplifier, a digital oscilloscope (Tektronics TDS520A, 500 MHz), and then stored in a personal computer for further processing.

We have carried out several checks prior to the measurement. First, we have sent the linearly polarized laser beam from one side of the dewar whose outer vessel is filled with liquid nitrogen, and detected the dye laser beam itself from the other side through a polarizer. We have confirmed that the polarization of the excitation laser beam is not destroyed ($>$99%) when it goes through four glass layers of the Pyrex dewar and liquid nitrogen. Second, by filling the outer vessel with liquid nitrogen but leaving the inner vessel in vacuum ($\sim 10^{-3}$ Torr), we have performed the laser ablation of Ba and detected $I_{\parallel}$ and $I_{\perp}$ of the LIF through the polarizers $p1$ and $p2$. In vacuum, polarization of the LIF should not be destroyed under the ideal situation, i.e., perfectly polarized excitation laser beam and no destruction of the polarization of the LIF when observed through the Pyrex wall and liquid nitrogen. We have used the transition from $5d6p\ ^3D_1$ to $6s5d\ ^3D_1$ for this check [see Fig. 1(a)]. We have observed that the ratio of $I_{\parallel}/I_{\perp}$ is about 8%. By taking into account the fact that 18% Ba with natural abundance has hyperfine structure (i.e., nuclear spin $I = 3/2$), this ratio agrees well with that under the ideal collision-free and no-instrumental-depolarization environment [9]. Thus we have confirmed that our experimental system does not suffer from any undesired instrumental depolarization within $<$1%. Having done the checks described above, we have moved on to the measurement of the time-resolved LIF signal of Ba under the He gas environment. Depending on the gas temperature desired for the measurement, the He gas has been introduced into the inner vessel of the dewar by two different ways. For the measurement below room but above the liquid nitrogen temperature, the He gas is flowed through the inner vessel. In order to achieve the He gas temperature below 77 K, the inner vessel of the dewar is partially filled with liquid He, above which the Ba sample is placed. By the continuous evacuation of the inner vessel with a rotary pump, the superfluidity of liquid He is maintained. The maintenance of the superfluidity is useful, since the evaporation of the liquid He is kept minimal. Thus the measurement can be performed under the stable He gas atmosphere without a rapid change of the local gas pressure, and the whole depolarization measurement described in this paper has been performed at the gas pressure of 2–6 Torr, which has been monitored by a capacitance manometer (MKS Baratron Model 626). Furthermore, we have scanned the monochromator from 350 nm to 900 nm under the dye-laser excitation in order to ensure that there are no energy-changing collisions taking place: If there were significant energy-changing collisions during the radiative lifetime of the laser-excited state, the time profile of the LIF signal will be distorted and the sensitized fluorescence will be observed at different wavelengths from that of LIF. It is believed that the cross sections for such energy-changing collisions are smaller than those for depolarizing collisions by two orders of magnitude or so, and should be negligible. We have indeed confirmed that energy-changing collisions are negligible for our measurement since we have not observed any detectable sensitized fluorescence in 300–

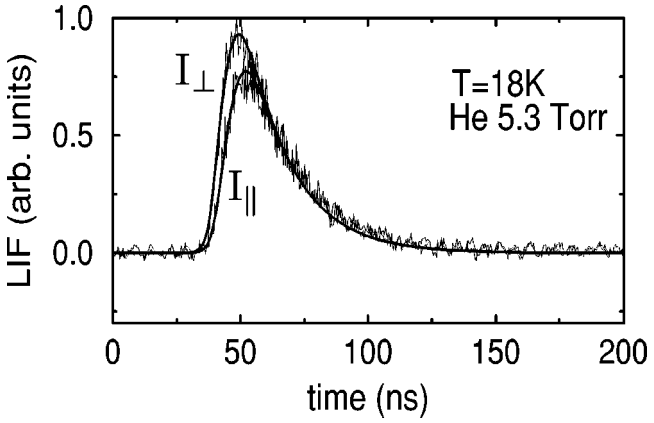

FIG. 3. Representative time profiles of the LIF and the fitted curves.

900 nm. The fact that the time profile of the LIF is not distorted also indicates that there is no radiation trapping effect.

In Fig. 3 we now show a representative result for the $5d6p\ ^3D_1$ state of Ba with 5.3 Torr He gas at 18 K. It can be easily shown that the $I_\parallel$ component is zero in vacuum for the $J=1$ to $J=1$ transition [3,9] if the hyperfine structure is ignored, and the growth of its intensity under the buffer gas environment indicates that the inequality of the population distribution among magnetic sublevels, i.e., alignment, is destroyed due to the population transfer among them. In order to determine the population transfer rate Γ_a, we employ a simple model that consists of one lower state $|J=0,\ m=0\rangle$ and three excited states $|J=1,m=0,\pm 1\rangle$ [see Fig. 1(b)] [3]. Assuming the time-varying excitation function $\Omega(t)$ by linearly polarized light, only the $|J=1,m=0\rangle$ sublevel is populated. With buffer gas, the population transfer among magnetic sublevels takes place as shown in Fig. 1(b) with the rates given by Γ_a (between $|J=1,m=0\rangle$ and $|J=1,m=\pm 1\rangle$) and Γ_b (between $|J=1,m=1\rangle$ and $|J=1,m=-1\rangle$). As stated before, the rate Γ_b cannot be determined from the present measurement. We solve a set of rate equations with four levels using a time-varying excitation function $\Omega(t)$, spontaneous decay rate, and a trial population transfer rate Γ_a [3]. In this way we can calculate the time evolution of the populations of upper states, from which the time evolution of the LIF, $I_\parallel(t)$ and $I_\perp(t)$, can be obtained. It should be noted that the excitation function $\Omega(t)$ has been obtained from the time-varying scattering signal of the dye laser beam. Thus we can avoid taking the convolution of the laser pulse shape and an instrumental function. By fitting the numerically obtained time-resolved LIF signal for each polarization component to the experimental one using a simplex method, we can determine Γ_a. We have again confirmed that there are no energy-changing collisions detectable within our experimental accuracy, since the decay rate of the excited state does not change with or without the buffer gas. Once Γ_a has been determined, we convert it to the depolarization cross section through the relation

$$\sigma_d(T)=3\Gamma_a(T)/[\bar{v}(T)n_{\mathrm{He}}], \tag{1}$$

where $\bar{v}=\sqrt{8k_BT/\pi\mu}$, with k_B and μ being the Boltzmann constant and the reduced mass of the Ba-He system, respectively. The factor 3 in the above formula comes from the conventional definition of the depolarization rate. In this paper, we have estimated the depolarization cross sections by assuming that Ba has no hyperfine structure. In reality, 18% of Ba used in our experiment has nuclear spin $I=3/2$. Note, however, that the corrections due to hyperfine structure are not important as long as the temperature dependence of the depolarization cross sections is concerned. From our recent study on the depolarization effects of $5d6p$ Ba with He at room temperature, the cross sections have been found to be overestimated by 20% if the hyperfine structure is neglected for the data analysis [3]. Therefore, if necessary, the cross sections including the hyperfine structure depolarization can be easily obtained by reducing them to 80% of the values reported in this paper [3].

Because of the use of laser ablation, however, there is one more important check to be made before the measurement for temperature dependence. Recall that this kind of experiment is usually performed under thermal equilibrium and an isotropic environment, which is easily guaranteed by the use of a heat pipe filled with buffer gas. In the present work, however, we have employed laser ablation for the creation of metal atoms below room temperature, and the ablated atoms have initially a nonthermal as well as nonisotropic velocity distribution. Whether the collision is occurring in a thermal and isotropic environment or not should be experimentally examined. For that purpose, we have measured the depolarization rate at a certain gas temperature and pressure as a function of delay time between the ablation and excitation pulses. We have found that there is practically no delay-time dependence within error bars in the delay range of 400–800 μs, which means that the collision is considered to be occurring under the thermal equilibrium. We have chosen the delay time of 500 μs for all measurements presented in this paper. Recalling that the distance between the sample and the excitation region is 1.5 cm, this choice of delay time is again found to be reasonable, since at the temperature of 10 K the thermal velocity of Ba atoms is about 35 m/s, which is comparable to the mean velocity of the Ba atoms coming into the excitation region from the sample with the present experimental geometry.

Having done this final check, we have repeated the measurements at different temperatures. The results are shown in Figs. 4(a) and 4(b) for $^3P_1$ and $^3D_1$ of Ba $5d6p$, respectively. It can be seen that the depolarization cross sections have positive temperature dependence for both states. The temperature dependence, however, seems to be stronger for $^3P_1$ than for $^3D_1$. It should be noted that the semiclassical impact parameter theory predicts the $T^{-1/(n-1)}$ dependence of depolarization cross section for an R^{-n} interaction potential [4]. Therefore, if the interaction potential is a van der Waals type, the temperature dependence should be represented by $T^{-1/5}$, which is contradictory to our results. We note that similar findings have been reported for the Ne-He systems [6,8], and the theoretical explanation has been given by Bahrim *et al.* [7] in terms of quasimolecular potential curves. As is well known, the detail of the electron density distribution does not matter if the depolarizing collision effectively occurs at a large internuclear distance, and the dynamics can be explained in terms of polarizability. As the collision distance becomes smaller, the deviation of the in-

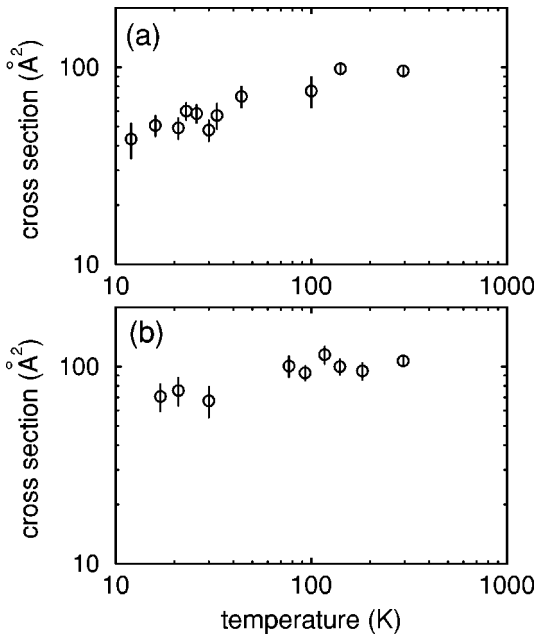

FIG. 4. Depolarization cross section of Ba (a) $5d6p\ ^3P_1$ and (b) $5d6p\ ^3D_1$ as a function of He gas temperature.

teraction from the van der Waals potential becomes larger and the dynamics should be discussed in terms of quasimolecular potential curves. Unfortunately, the Ba-He potential curves reported in the literature are only for Ba $6s^2$, $6s5d$, and $6s6p$ [10], and to our knowledge there is no study for Ba $5d6p$.

In order to understand our results, at least qualitatively, we calculate the approximate electron density distribution of the $5d6p\ ^3P_1$ and $^3D_1$. The Hartree-Fock calculations including several configurations suggest that those states have very small configuration mixing with other states, and can be well described by a single LS state with $>95\%$ purity. The mean radii of the $5d$ and $6p$ electrons for the configuration-averaged $5d6p$ states are calculated to be 3.5 (a.u.) and 7.5 (a.u.), respectively. For comparison, the radii of the $5s$ and $5p$ core electrons are 1.7 (a.u.) and 1.9 (a.u.), respectively. Starting from an LS-coupled two-electron wave function $\Psi^{\Omega}_{nln'l'}$ and expanding it by LS-uncoupled wave functions $\Psi^{\Lambda}_{nln'l'}$ [11], we obtain

$$\Psi^{\Omega}_{nln'l'}=\sum_{M_S M}(-1)^{L-S}\sqrt{2J+1}\begin{pmatrix} S & L & J \\ M_S & M & -M_J \end{pmatrix}\Psi^{\Lambda}_{nln'l'}, \tag{2}$$

where we have introduced two sets of quantum numbers $\Omega=(SLJM_J)$ and $\Lambda=(SLM_SM)$. By further introducing the antisymmetrized wave functions, we can express $\Psi^{\Lambda}_{nln'l'}$ as

$$\Psi^{\Lambda}_{nln'l'}=\sum_{mm'}\sum_{m_s m_s'}(-1)^{l'-l}\sqrt{(2S+1)(2L+1)} \times\begin{pmatrix} l & l' & L \\ m & m' & -M \end{pmatrix}\begin{pmatrix} l/2 & 1/2 & S \\ m_s & m_s' & -M_S \end{pmatrix} \times\phi^{mm_s m' m_s'}_{nln'l'}(\vec{r}_1,\vec{r}_2) \tag{3}$$

with $\phi^{mm_s m' m_s'}_{nln'l'}(\vec{r}_1,\vec{r}_2)$ being the usual Slater determinant of the orbital u_{nlmm_s}. Following the procedure briefly described above, and integrating over the spatial coordinates of $\vec{r}_2$ (or $\vec{r}_1$), we can calculate the density distribution of the valence electron, which is a superposition of the $5d$ and $6p$ wave functions. The results are plotted in Fig. 5 at the radius of 7.5 (a.u.), where the weighting factor 5 comes from the difference of probability density between $5d$ and $6p$ electrons at 7.5 (a.u.). It can be seen that the electron density distribution is closer to spherical for $^3P_1$ than $^3D_1$, implying that the interaction with He is more repulsive for $^3P_1$ than for $^3D_1$ around the internuclear distance of 7.5 (a.u.) or larger, since the $6p$ electron is responsible for collisions. Indeed, more repulsive interaction leads to a stronger positive temperature dependence of depolarization cross section. On the other hand, when the He gas temperature is high, collisions occurring at a large internuclear distance effectively determine the depolarization cross section, and the detail of

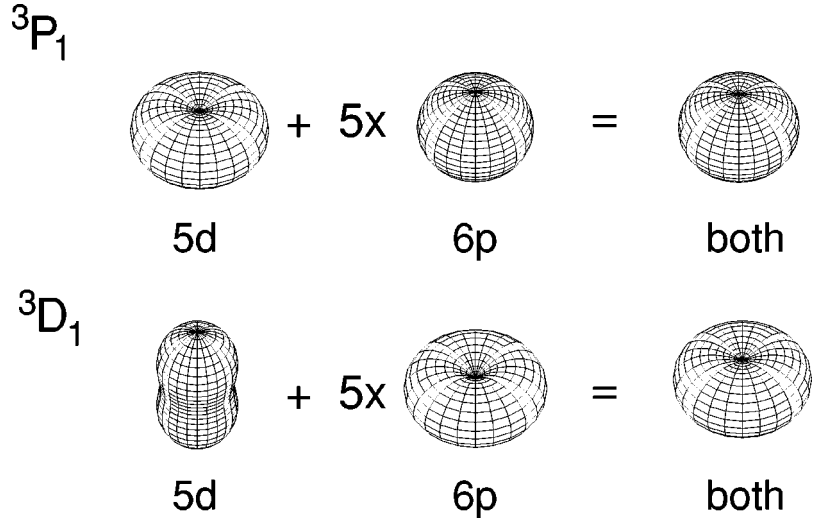

FIG. 5. Approximate electron density distribution for $5d6p\ ^3P_1$ and $5d6p\ ^3D_1$ at radius $r=7.5$ (a.u.). The factor 5 comes from the ratio of probability density of $5d$ and $6p$ electron at $r=7.5$ (a.u.).

the electron density distribution should not matter, as predicted by the impact parameter theory [4]. Although our tentative argument does not take into account the interaction with He atoms, it still explains the qualitative feature of the depolarizing cross section at lower temperature. For the quantitative understanding of the observed temperature dependence, however, a detailed theoretical study will be necessary.

In summary, we have measured the temperature dependence of the depolarization cross sections of the $5d6p\ ^3P_1$ and $^3D_1$ states of Ba in He gas in the wide temperature range 10–300 K. The measurement at the temperature as low as 10 K has become possible by the use of the laser-ablation technique. We have found that the depolarization cross sections have a positive temperature dependence for both states. The temperature dependence, however, has turned out to be stronger for $^3P_1$ than $^3D_1$. Since there is no theoretical study related to our scheme involving the doubly excited $5d6p$ states of Ba, we have given a tentative and qualitative interpretation for this difference in terms of the electron density distribution.

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