Stark beats of Ar Rydberg states

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Vacuum ultraviolet fluorescence decay spectra of Ar atom resonance lines excited by pulsed vacuum ultraviolet light in a synchrotron single bunch operation were obtained under a static electric field. When an atom under the static electric field was excited simultaneously to both the magnetic sublevels $M=0$ and $|M|=1$ by polarized light and the observation area was asymmetric, Stark beats were observed in the fluorescent decay spectra. All observed beat frequencies varied proportionally to the square of the external electric field. The results for $8d$ and $9d$ doublet lines were compared with those obtained by the usual second order perturbation theory, assuming mixing ratios between three jl coupling scheme d-type states. The beat frequencies were also measured for other resonance lines.

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I. INTRODUCTION

The Stark effect in Ar Rydberg states has been studied using the collinear laser spectroscopy technique in the vicinity of the $n=18$ hydrogen manifold below the first ionization limit [$(3p^5)^2P_{3/2}$ ionic core] [1]. Stark effect studies with laser spectroscopy have been performed for Kr and Xe atoms in the ionization region where autoionization takes place [2–4]. Synchrotron radiation has also been used to study the Stark effect of Kr below the ionization limit [5]. All studies show that the spectral line positions and intensities of the Stark manifolds are well explained by the jl coupling scheme.

The Stark shift is generally small compared with the Zeeman shift. Furthermore, Stark splitting between the $M=0$ and $|M|=1$ levels is much smaller than the Stark shift. Therefore, we cannot detect the splitting with a conventional vacuum spectrometer and ordinary electric field strength (1–10 kV/cm). However, if beating caused by interference between the two levels occurs, we can deduce the energy splitting by converting the beat frequency even if the splitting is very small, and we may estimate the Stark shift from the energy splitting.

Stark beat studies for hydrogen [6–8], alkali metals [9–12], Ba [13], alkali hydrides [14,15], pyrimidine [16], and many other molecules have been performed with beam foil spectroscopy and pulsed dye laser excitation. However, as far as we know, there have been no rare gas Stark beats observed in the vacuum ultraviolet. The observation was impossible due to lack of a vacuum ultraviolet radiation source strong enough for fluorescence study. After observing the lifetimes of Ar resonant Rydberg states, we noticed that the life time values vary between a few nanoseconds and 1 μsec and predicted that the lifetimes of some states would be suitable for beat period measurements using an appropriate electric field strength. We attempted Stark beat measurements for several Ar Rydberg states and succeeded.

Although laser radiation can be applied to rare gas Stark effect measurement, synchrotron radiation single bunch operation is more convenient in energy ranges wider than that of a laser, in spite of its poor energy resolution.

II. EXPERIMENTAL METHOD

The experiments were performed on beamline 20A of the Photon Factory at the Institute of Materials Structure Science of the High Energy Accelerator Research Organization located in Tsukuba, Japan. A 3 m normal incidence monochromator [17] equipped with a 2400 lines/mm grating was used. A photon bandwidth of 0.03 Å was obtained with a slit width of 10 μm and the monochromatized light was considered to be polarized, although we did not measure the polarizability. The synchrotron radiation in a single bunch operation had a pulse width of approximately 50 psec and a repetition period of 624 nsec.

Figure 1 shows a schematic diagram of the experimental apparatus. The applied Stark electric field electrodes consisted of gold mesh and were separated from each other by 11 mm. The center of the electrode corresponds to the interaction region. A 30 μm diameter supersonic gas nozzle was located at a distance of about 21 mm from the interaction region. The vacuum chamber was evacuated with a cryopump, at a speed of 20 000 l/s, maintaining a background pressure of 1×10^{-5} Torr in the presence of the gas beam.

We take the electric field direction as the z axis and the light beam as the y axis. The x axis is the molecular beam axis which is parallel to the electrodes. The vacuum ultraviolet fluorescence detector microchannel plate was placed over the mesh electrode. Half of the fluorescence observation was blocked by a wall as seen in Fig. 1. Therefore, the direction of fluorescence observation was slanted in relation to the y-z plane. The electric field strength can be increased to 5 kV per 1.1 cm in the present setup. The voltage is supplied continuously and hence there is always a finite electric field present in the interaction region. The light polarization directions were slanted at 45° and $-45°$ from the z axis on the z-x plane.

The true value of the electric field strength and hence the

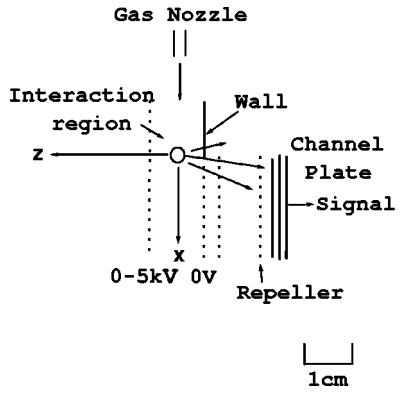

FIG. 1. Schematic of the experimental apparatus. Applied Stark electric field electrodes consisted of gold mesh and were separated from each other by 11 mm. The center of the electrodes corresponds to the interaction region. The VUV fluorescence detector microchannel plate was placed over the mesh electrode and half of the fluorescence observation was blocked by a wall. We take the electric field direction as the *Z* axis and the light beam as the *Y* axis. The *X* axis was the molecular beam axis. Therefore, the direction of fluorescence observation and the electric field are always invariant. A supersonic gas nozzle of 30 μm diameter was located at a distance of about 21 mm from the interaction region. The electric field strength can be increased to 5 kV per 1.1 cm in the present setup.

effective distance between electrodes was calibrated by measuring the He $4\,^1P_1$ resonance line Stark beat frequency, which was calculated by the second order perturbation method. As a result, we used an electrode interval of 11.45 mm instead of the measured value 11.0 mm. The measured Stark beat frequencies for the He resonance line using the calibrated electric field strength and other resonance lines and the calculated results are shown in Table I. These values for the $4\,^1P_1$ and $5\,^1P_1$ lines were confirmed by comparing the results obtained using secular equations used previously [18].

The wavelength calibration and hence the energy calibration were performed by comparing the peak energy values with the previous study [19]; the peak energy values of the Ar Rydberg states agreed well with those in the previous study.

TABLE I. He resonance line Stark beat frequencies in a 1 kV/cm electric field were calculated by the second order perturbation method. The values are measured using the electric field obtained by assuming that the calculated $4\,^1P_1$ line beat frequency is correct.

Energy level	Calculated frequencies (MHz)	Measured values (MHz)	Ratio (measured/cal.)
$3\,^1P_1$	5.72	6.87	1.201
$4\,^1P_1$	51.69	51.69[a]	1.000
$5\,^1P_1$	265.74	271.40	1.021
$6\,^1P_1$	989.40	1021.70	1.033
$7\,^1P_1$	2946.00	2842.40	0.965
$8\,^1P_1$	7878.00	7524.20	0.955

[a]This value was fitted to the calculated value.

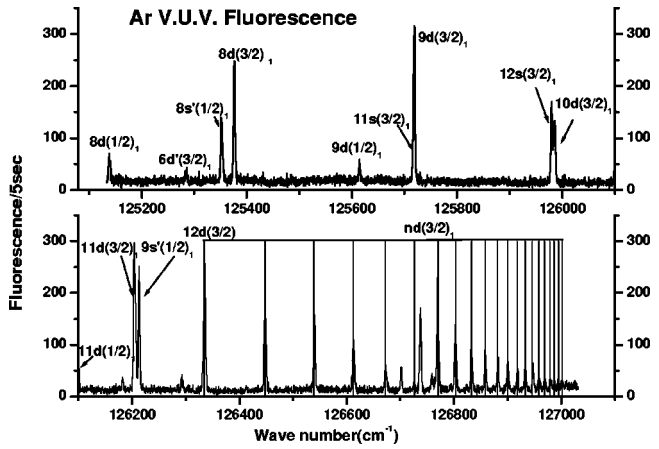

FIG. 2. The fluorescence spectrum between the $8d(1/2)_1$ line and a wavelength near the first ionization limit is shown. The line assignment was performed by referring to Yoshino [19]. This spectrum was obtained under electric-field-free conditions and with slit widths of 10 μm. $9d(3/2)_1$ and $11s(3/2)_1$ lines overlap in the present study. However, the $11s(3/2)_1$ line intensity is assumed to be very weak, because $10s(3/2)_1$ cannot be recognized in the present spectrum.

III. RESULTS AND DISCUSSION

The fluorescence spectrum between the $8d(1/2)_1$ line and a wavelength near the first ionization limit is shown in Fig. 2. The line assignment was performed by referring to Yoshino [19]. This spectrum was obtained under field-free conditions and with a slit width of 10 μm corresponding to a resolution of 0.03 Å. Lines having strong fluorescent intensity were selected for beat measurements. The $10s(3/2)_1$ line cannot be observed in the present experiment. Since the $9d(3/2)_1$ and $11s(3/2)_1$ lines are separated by only 0.017 Å [19], we could not separate these lines nor find the shoulder of the $11s(3/2)_1$ line. Since the $10s(3/2)_1$ line did not appear, the intensity of the $11s(3/2)_1$ line is considered to be very weak or missing. We tentatively identified the 125718 cm^{-1} emission line as $9d(3/2)_1$. The $10d(3/2)_1$ and $12s(3/2)_1$ lines also overlapped in the present resolution.

The fluorescence Stark beat spectrum of the Ar $9d(3/2)_1$ state observed is shown in Fig. 3. The dotted line was obtained under an 885 V/cm electric field. The beat frequency under the electric field was 358 MHz.

The Stark $|\Delta M|=1$ quantum beat intensity was derived as follows by using Eq. (8) in Ref. [16],

$$I_f(\omega_b) \propto \epsilon_x \epsilon_z \lambda_x \lambda_z \exp(-\Gamma t)\cos(\omega_b t) \times |\langle \gamma_e J_e \| \mu \| \gamma_i J_i \rangle|^2 |\langle \gamma_e J_e \| \mu \| \gamma_f J_f \rangle|^2 \qquad (1)$$

where $\langle \gamma_e J_e|$, $|\gamma_i J_i\rangle$, and $|\gamma_f J_f\rangle$ denote the excited, initial, and final states, respectively. Γ is the decay constant of the excited states and ω_b is the angular frequency corresponding to the energy separation between $|e\rangle$ and $|e'\rangle$, which correspond to the $|M|=0$ and 1 sublevels. ϵ_x and ϵ_z are photon electric field amplitudes in the x and z directions, respectively. λ_x and λ_z are the direction cosines that specify the polarization direction of the observed fluorescence. Since the light polarization direction was slanted by approximately 45°

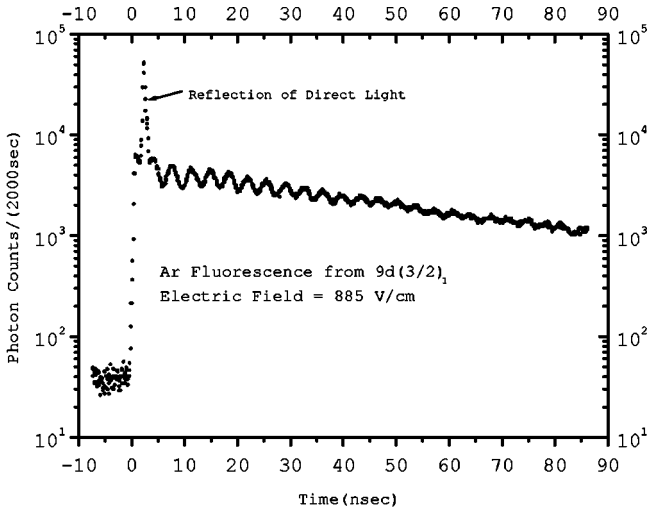

FIG. 3. The fluorescence decay spectrum of the Ar $9d(3/2)_1$ state was observed. The electric field was slanted by 45° to the radiation polarization directions. In this case the Ar atom is excited to $|M|=0$ and 1 sublevels from the ground state with only $M=0$. The dotted line was obtained under an 885 V/cm electric field.

from the z axis, we have nonvanishing ϵ_x and ϵ_z. The factor $\lambda_x\lambda_z$ has opposite signs for fluorescence emitted to one side and the other of the y-z plane. This means that fluorescence emissions to different sides are beat signals with opposite phases, which cancel each other if they are detected simultaneously. Therefore, observation of $|\Delta M|=1$ quantum beats requires detection asymmetric to the y-z plane. In the present experiment, we blocked half of the fluorescence (the $-x$ part) using a wall as can be seen in Fig. 1.

The spectrum measured under the same electric field and with polarization radiation slanted by $-45°$ to the z axis is shown in Fig. 4. With 90° rotation of the radiation polarization, the sign of $\epsilon_x\epsilon_z$ in Eq. (1) changes. The sign of $\lambda_x\lambda_z$ is

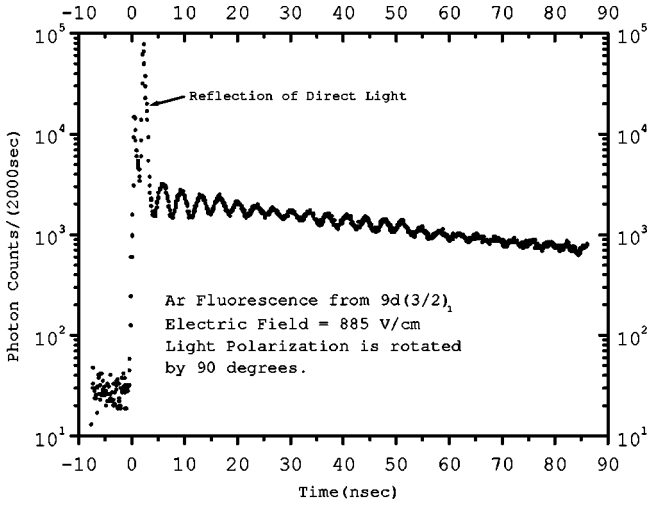

FIG. 4. The fluorescence decay spectrum of the Ar $9d(3/2)_1$ state was observed. The electric field was slanted by $-45°$ to the radiation polarization direction. The dotted line was obtained under an 885 V/cm electric field.

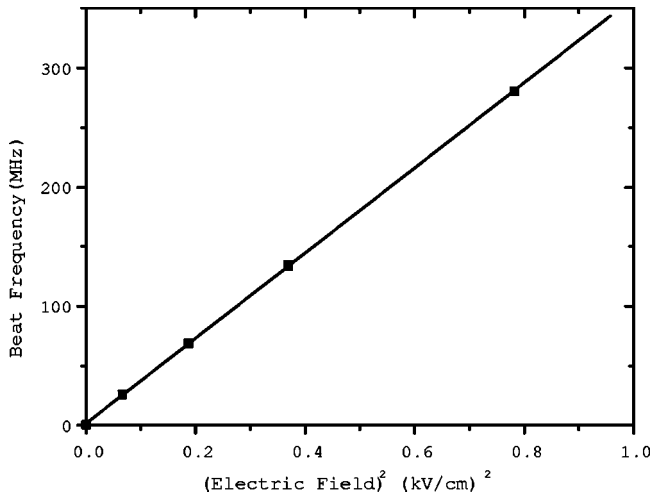

FIG. 5. The $9d(3/2)_1$ beat frequencies versus the square of the electric field strength are shown. It is clear that the frequency depends on the square of the electric field strength.

unchanged, because the Stark electric field direction was taken as the z axis and thus the coordinates of the observation direction and the Stark electric field direction are invariant for rotation of the excitation light polarization. According to Eq. (1), the beat intensity $I_f(\omega_b)$ changes sign. The observation signal was inverted as seen in Fig. 4. A small discrepancy (3%) in the frequencies exists between Figs. 3 and 4. This is due to the small variation (1.5%) of the electric field caused by the rotation, that is, by the fact that the electric field was not uniform and the position of the interaction region was accidentally shifted.

Figure 5 shows the $9d(3/2)_1$ beat frequency electric field dependence. It is clear that the frequency depends on the square of the electric field strength. Since the Ar atom is excited to the $|M|=0$ and 1 sublevels from a ground state having only the $M=0$ level, this Stark beat is explained by second order perturbation theory in which the magnetic quantum number M degeneracy is resolved. The energy displacement ΔE is expressed as follows ([20], p. 411):

TABLE II. Assumed mixing coefficients, calculated beat frequencies, and observed values for a 1 kV/cm electric field.

Energy level	Mixing coefficient $d'(3/2)_1$	$d(1/2)_1$	$d(3/2)_1$	Calculated frequency (MHz)	Observed value (MHz)
$8d(1/2)_1$	$+0.500$[a]	$+0.281$	$+0.819$	490	490
$8d(1/2)_1$[b]	$+0.479$	-0.609	$+0.632$	4188	
$8d(3/2)_1$	$+0.500$[a]	$+0.768$	-0.400	1528	1528
$8d(3/2)_1$[b]	$+0.590$	$+0.799$	$+0.119$	675	
$9d(1/2)_1$	$+0.000$[a]	$+0.458$	$+0.889$	246	246
$9d(1/2)_1$[b]	$+0.241$	-0.484	$+0.842$	1552	
$9d(3/2)_1$	$+0.000$[a]	$+0.963$	-0.270	358	357
$9d(3/2)_1$[b]	-0.146	$+0.836$	$+0.529$	1632	

[a]Postulated.

[b]Calculated using the parameters of Lee and Lu [24].

TABLE III. The calculated results for the Stark shifts and separations (1 kV/cm) of Ar resonance lines in the jl and experimental results (1 kV/cm). Experimental error was 5%.

Energy level	Wave number (cm^{-1})[b]	Stark shift $(M=0)$ (cm^{-1})	$(M=\pm1)$	ΔM[a] splitting (cm^{-1})	(MHz)	Experiment (MHz)
$8d(3/2)_1$	125376.9	−0.21000	−0.28830	−0.02830	−849	1528
$9d(3/2)_1$	125718.1	−0.13400	−0.14753	−0.01353	−406	357
$10d(3/2)_1$	125979.4	−0.21817	−0.24632	−0.02816	−845	723
$11d(3/2)_1$	126204.1	+4.08342	+3.61055	−0.47287	−14186	15 040
$12d(3/2)_1$	126334.2	[c]				17 600
$13d(3/2)_1$	126447.9	[c]				4940
$8d(1/2)_1$	125135.8	+0.09549	+0.00912	−0.08637	−2591	490
$9d(1/2)_1$	125613.1	+0.02116	−0.00562	−0.02679	−804	246
$11d(1/2)_1$	126099.4	[c]				68 000
$8s'(1/2)_1$	125353.1	[c]				36.4
$9s'(1/2)_1$	126211.6	[c]				800

[a] $E_{M=\pm1}-E_{M=0}$.
[b] From Ref. [19].
[c] Calculation was not performed.

$$\Delta E(\alpha JM)=\varepsilon^2[J^2a_-+(J+1)^2a_+-(a_++a_--a_0)M^2]. \tag{2}$$

Here, ε is the electric field strength and

$$a_-=\sum_\beta \frac{|(\alpha J|ez|\beta J-1)|^2}{(E_{\alpha J}-E_{\beta J-1})} \tag{3}$$

represents the perturbation caused by the levels for which $J'=J-1$; a_0 and a_+ are similar expressions for the perturbation caused by levels of $J'=J$ and $J+1$, respectively. The matrix components were calculated using the equation in the jl scheme [Eq. (2) in Ref. [2]], tables for the computation of radial integrals in the Coulomb approximation [21] and the p and f state energies [22]. The resulting energy splitting between the $M=0$ and $|M|=1$ levels of $9d(3/2)_1$ corresponding to the 1 kV/cm electric field strength was 411.0 MHz, assuming that this state includes only $d(3/2)$ character. This nearly agrees with our experimental result of 357 ± 18 MHz (the 5% error is mainly due to the 2% uncertainty in the electric field strength). For $8d(1/2)_1$ and $(3/2)_1$ and $9d(1/2)_1$, we calculated the beat frequencies. However, the agreement between the experimental and calculated results was not good. Therefore, we determined the $8d$ and $9d$ mixing coefficients of $d'(3/2)$, $d(1/2)$, and $d(3/2)$, so that the observed values fitted the calculated ones, assuming that $8d$ mixes with $d'(3/2)$ at 25% and $9d$ has no mixing with $d'(3/2)$, and that p and f states have no mixing, which is supported by Ref. [23]. The assumption that $8d$ mixes with $d'(3/2)$ at 25% is near the results obtained using the multichannel quantum defect theory (MQDT) parameters of Lee and Lu [24]. The results are shown in Table II. From the mixing ratio, we can see that the previous $(1/2)_1$ and $(3/2)_1$ assignments should be converted. MQDT analysis using the parameters of Lee and Lu [24] supports our results except for the plus-minus sign.

We also measured the beat frequencies for the $10d-13d(3/2)_1$, $11d(1/2)_1$, $8s'$, and $9s'(1/2)_1$ levels. The results are shown in Table III.

IV. SUMMARY

A vacuum ultraviolet fluorescence measurement was performed for the Ar atom in a synchrotron single bunch operation. The beat frequencies varied proportionally to the square of the external electric field. These frequencies were compared with the results obtained by the usual second order perturbation theory. For Ar atom resonance lines of $8d$ and $9d(1/2)_1$ and $(3/2)_1$, the beat frequencies were calculated. The results corresponded to those of the second order perturbation theory on including $d'(3/2)$, $d(1/2)$, and $d(3/2)$ mixing.

Stark beat spectroscopy using polarized synchrotron radiation, which we call SRIF (synchrotron radiation induced fluorescence), can begin now because using this method we can test the usefulness of second order perturbation theory in a weak electric field and determine whether or not the wave functions are appropriate.

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