Effects of very low electric fields on narrow autoionizing states in gadolinium

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We have observed a narrow (0.075-cm^{-1}) isolated autoionizing level to undergo a stepwide increase in width at an electric field strength ~ 2 V/cm. At such low fields, classical field ionization or "forced autoionization" cannot account for this phenomena. We find that the autoionizing level is narrow because of its high angular momentum ($J=5$). The level is energetically embedded in the Rydberg series converging to a nearby limit. The model we propose suggests that such narrow autoionizing levels will increase in width near a field $F\,(\text{a.u.})=\frac{1}{3}n^5$ for n values of the Rydberg levels which lie nearby in energy. At this field (Ingliss-Teller limit), adjacent n Stark manifolds begin to overlap, resulting in the onset of complete "l mixing."

I. INTRODUCTION

Several years ago,[1] a narrow even-parity autoionizing state was observed in gadolinium lying approximately 230 cm^{-1} above the first ionization limit. Two interesting features of this state were noted, namely, its narrow width (0.075 cm^{-1}, corresponding to a decay time of 4.4×10^{-10} sec) and the fact that the observed line broadened to ~ 0.35 cm^{-1} when a field of 100 V/cm was applied to the interaction region. In order to obtain more information on the field dependence of this state, as well as to possibly provide some explanation of both its narrow width and why it is broadened by weak fields, a more detailed study of the spectral region within ~ 10 cm^{-1} of the observed state has been carried out using essentially the same three-step excitation techniques. The original measurements have been extended by using additional pumping schemes in order to determine the J value of the autoionizing state.

We have observed the width of this narrow autoionizing level to remain roughly constant up to a field strength of about 2 V/cm, and then increase rapidly to a new plateau. The field-enhanced width is about four times larger than the zero-field width. The effects we observe are at a much lower field strength than that required for classical field ionization ("forced" autoionization). An exploration of the opposite parity in the same spectral range was made in order to determine whether there were odd parity states in the same spectral range which might account for the weak-field broadening. Rydberg series converging to the first excited state of the ion were found and their field dependence was also studied.

We hypothesize that the field enhancement of the width stems from the fact that the observed level is embedded in high-n levels of the Rydberg series which converge to a nearby excited state of the ion. The electric field causes the sublevels of each Rydberg n level to "fan out" in energy and form a so-called Stark manifold. The model we present below predicts that the change in width should occur in the "n-mixing" region (Ingliss-Teller limit) for the Rydberg levels which lie near in energy to the level in question. That is, this occurs at fields where the Rydberg Stark manifolds from adjacent n levels overlap, with the subsequent strong mixing of the lower-angular-momentum states with the higher ones.

II. PUMPING SCHEMES AND EXPERIMENTAL PROCEDURES

The ionization potential of gadolinium is $49\,603\pm5$ cm^{-1} above the $4f^75d\,6s^2\,{}^9D_2^\circ$ ground state, and corresponds to the Gd II $4f^75d\,6s\ {}^{10}D_{5/2}^\circ$ ground state.[2] In order to excite even levels of gadolinium in the energy range above this limit several alternative pumping schemes were used as shown in Fig. 1. All of these alternative three-step processes used the $4f^75d\,6s\,6p\ {}^9D$ and $5f^75d\,6s\,7s\ {}^9D^\circ$ terms as intermediate states but utilized different levels of these terms and of the ${}^9D^\circ$ ground term. The purpose of this procedure was to determine the J value of the autoionizing state.

In order to obtain information on states of odd parity which the electric field might mix with even parity states in this spectral range, spectra were also taken via two-step excitation. The intermediate state in this case was the $4f^75d^26p\ {}^{11}D_5$ level which was excited from the $J=4$ level of the ground term.

The experimental technique used here is similar to that used previously to study field effects in barium.[3] A beam of gadolinium atoms from a 1650-K oven was collimated and passed through field plates 1 cm apart. This beam was crossed at right angles with three laser beams from dye lasers tuned to transitions appropriate to the particular pumping scheme being used. The three laser beams were made nearly collinear by imaging them separately onto a spherical mirror in such a way that they overlapped in the interaction region.

The dye lasers were pumped by a Nd:YAG laser (where YAG denotes yttrium aluminum garnet) operated at 10 Hz with an 8-nsec pulse duration. Two grazing-incidence dye lasers with prism beam expanders and 0.1-cm^{-1} bandwidth were used to excite the upper bound levels. A third dye laser with intracavity etalon was used for the final transition to the autoionizing resonance. This laser,

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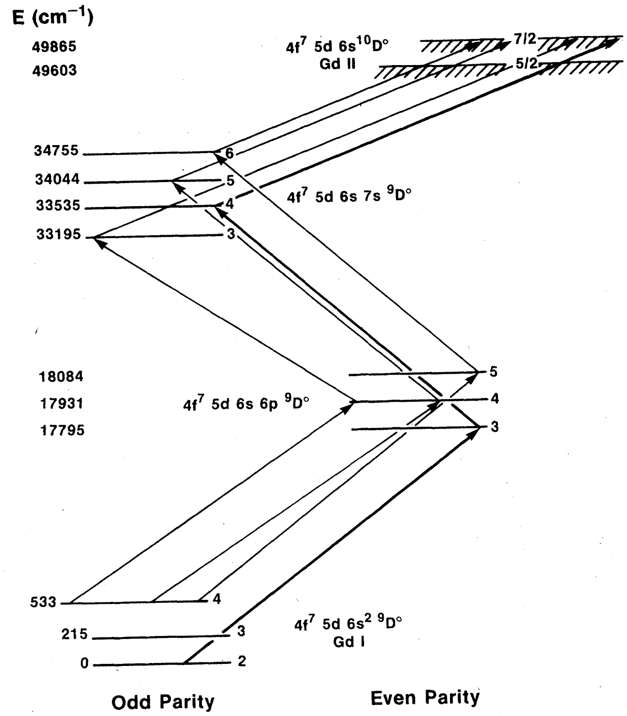

FIG. 1. Pumping schemes used for three-step excitation. The heavier solid line indicates the scheme used in Ref. 1, and the scheme used by us to study the field effects. The observed spectral region lies about 29 cm^{-1} below the $^{10}D_{7/2}$ limit of Gd^+.

which has a 0.03-cm^{-1} bandwidth, was pressure scanned with nitrogen for small tuning ranges, and with Freon 12 for larger ranges. Ions, formed by autoionization in the region between the plates where the beams cross, passed through a fine metal screen in one of the 4-in. plates and were detected with an EMI D233B electron multiplier with a linear array of 14 dynodes. The signal from the multiplier was sent to the input of a boxcar averager with digital memory. The time constant of the averager was small compared to the scanning speed of the dye laser. The stray field from the electron-multiplier voltage was inferred to be on the order of 0.1—0.3 V, based on the reverse-bias voltage required to suppress ion collection.

The first two lasers, used to reach the excited states indicated in Fig. 1, were kept fixed in wavelength; their pulse energy was adjusted to be high enough to saturate the transitions to the bound levels, but not so strong that they led to significant photoionization of the highly excited bound state. The small background ionization signal from this process could be measured by blocking the third laser. Scans were made at various fixed values of electric field. The power of the final-stage dye laser was kept low to avoid depletion broadening. The laser bandwidth of the scanning laser, 0.03 cm^{-1}, was deconvolved from the measured one by assuming that the laser profile was Gaussian (G) and the autoionization profile was a symmetric Lorentzian (L). For $L \gtrsim 2G$, the convolved width V of the Voight profile is well approximated by $V=[L^{3/2}+G^{3/2}]^{2/3}$.

The wave-number calibration was made by shining the third laser in a hollow cathode discharge and detecting the resulting optogalvanic signals of neon lines. Displacements from the known wavelengths of neon[4] were measured with a Fabry-Perot étalon.

III. SPECTRA FOR STATES OF EVEN AND ODD PARITY

A spectrum in the range from 49 830 to 49 841 cm^{-1} above the ground state of gadolinium, obtained by three-step excitation, is shown in Fig. 2(a). The spectrum consists of the very narrow resonance reported in Ref. 1, and an additional weak structure which could not be identified. This measurement established the position of the previously observed autoionizing state as 49 836.0±0.2 cm^{-1} above the ground state. Results for the same level obtained via the $J=4\to4\to5$ and $4\to5\to6$ intermediate states were 49 836.0 and 49 835.9 cm^{-1}, respectively. Since dipole-selection rules should apply (in zero field) to the final-step excitation, these results, together with the fact that no lines are observed in this spectral region for $J=4\to4\to3$ intermediate states, indicate a J value of 5 for the 49 836.0-cm^{-1} level.

The zero field width of the $J=5$ even parity line at 49 836 cm^{-1} was measured to be 0.075 cm^{-1}, in agreement with Ref. 1. One would expect lines of high J value to have small autoionization widths owing to the following considerations. The only level of Gd^+ which can be reached by an autoionization process in this energy range is the $4f^7 5d\,6s\ ^{10}D^{\circ}_{5/2}$ ground state. For autoionization to occur in a state with $J=5$, the emitted electron must carry away angular momentum of at least $\frac{5}{2}$. Potential barrier effects will thus limit the autoionization width of states with $J \geqq 5$, since the emitted electron must have $J \geqq \frac{5}{2}$.

The spectrum obtained via $4\to5$ intermediate states to states of odd parity is shown in Fig. 2(b). Since this was the only scheme used for odd-parity excitation it was not possible to identify the J values of the states observed.

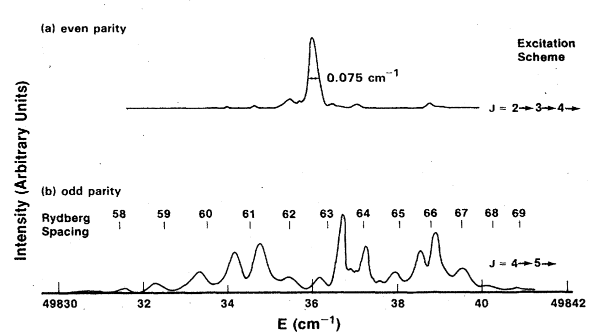

FIG. 2. Spectra obtained in the energy range 49 830—49 841 cm^{-1} via (a) three-step excitation to even-parity autoionizing states. Excitation is via the $J=2\to3\to4$ levels indicated in Fig. 1. (b) Two-step excitation to odd-parity autoionizing states.

TABLE I. Possible Rydberg series of the form nl_j of even parity converging to the $J=\frac{7}{2}$ limit of the Gd^+ ground term.

$J=4$		$J=5$		$J=6$	
l	j	l	j	l	j
0	$\frac{1}{2}$				
2	$\frac{3}{2},\frac{5}{2}$	2	$\frac{3}{2},\frac{5}{2}$	2	$\frac{5}{2}$
4	$\frac{7}{2},\frac{9}{2}$	4	$\frac{7}{2},\frac{9}{2}$	4	$\frac{7}{2},\frac{9}{2}$
6	$\frac{11}{2},\frac{13}{2}$	6	$\frac{11}{2},\frac{13}{2}$	6	$\frac{11}{2},\frac{13}{2}$
8	$\frac{15}{2}$	8	$\frac{15}{2},\frac{17}{2}$	8	$\frac{15}{2},\frac{17}{2}$
				10	$\frac{9}{2}$

Note that several of the strongest lines observed lie close to those observed in the even-parity spectra excited via three-step excitation. The spectrum contains 15 peaks of approximately the same width which have approximately the spacing expected for a Rydberg series converging to the $J=\frac{7}{2}$ limit. However, there are more peaks than one would expect for a Rydberg series and the intensity of the spectrum is concentrated in three regions. Our interpretation of this spectrum assumes that there are three interloping levels in this spectral range which mix strongly with one or more Rydberg series converging to the $^{10}D^{\circ}_{7/2}$ level of Gd^+. It is not possible to make a configuration assignment for this series. Since states with $J=4$, 5, or 6 can all be reached via single-photon excitation from the $J=5$ state, there will be 24 possible Rydberg series, eight for each J value, as shown in Table I. Note that only if $J=4$ is excited is it possible to have a series with the configuration $4f^7 5d\,5s\,{}^9D^{\circ}\,ns_{1/2}$. All of the other possible series have $l \geqq 2$. The most likely assignment, if this is in fact a perturbed Rydberg series, will be $4f^7 5d\,5s\,{}^9D^{\circ}_{7/2}\,nd$ with $J=5$ or 6. The spacing of unperturbed Rydberg levels for $n=58$–69 is shown in Fig. 2(b), the positions having been adjusted to give a reasonable fit to the data. It should be noted that this adjustment is somewhat arbitrary and is presented merely to point out that the spacing of levels is approximately that of a Rydberg series with n values in this range. Nevertheless, the adjustment, coupled with the known spacing of the $J=\frac{5}{2}$ and $\frac{7}{2}$ levels of Gd^+ ground state yields an ionization potential of 49 602.1 cm^{-1} in agreement with previous results.[1,2]

According to the above analysis the configuration mixing between even-parity Rydberg levels with each of the three perturbing levels is quite strong and we attribute the fact that we see so many lines in this spectral region to this strong mixing. The intensity of the observed structure fits this picture. Since the probability of exciting high-n Rydberg levels from low-n levels is quite small, they are observable mainly because they mix with the perturbing levels which presumably have a larger probability of excitation.

IV. FIELD-INDUCED BROADENING

The field effects on the odd-parity spectra of Fig. 2(b) are shown in Fig. 3. As in Fig. 2(b), 15 peaks are present at zero field. In Fig. 3, at a field of 1.27 V/cm some of these 15 levels have disappeared and the weaker spectral features have broadened. When the field is increased to 4 V/cm only three peaks remain as shown in Fig. 4(c). In zero field, each Rydberg n level is $2n^2$ degenerate. The electric field splits this degeneracy and causes each n level to fan out into a Rydberg "manifold" as the field increases. Below, after pointing out that the observed effects at such low fields cannot be due to classical field ionization, we attribute the field effects to phenomena which occur when the Stark manifolds of adjacent n levels overlap.

As mentioned earlier, the region studied lies only 29 cm^{-1} below the first excited level of Gd^+ (the $^{10}D^{\circ}_{7/2}$ level). Classically, the ionization limit will be "lowered" by an energy $E=6.1\sqrt{F}$ cm^{-1} for a field F expressed in

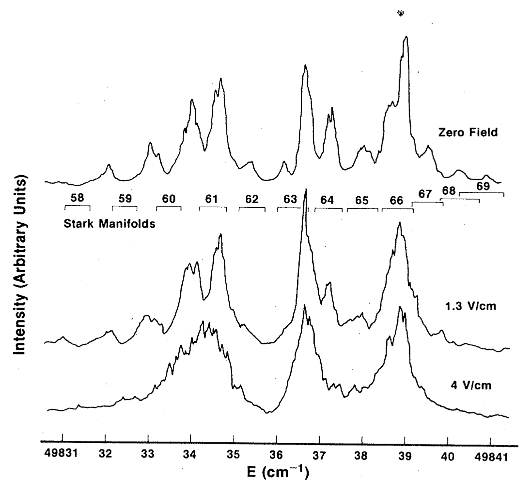

FIG. 3. Spectra obtained using 4⟶5 excitation; (a) zero field; (b) with a field of 1.27 V/cm; (c) with a field of 4 V/cm. The approximate "width" of the Rydberg manifold (i.e., the energy separation between the highest and lowest parabolic states) at 1.3 V/cm is indicated for each n.

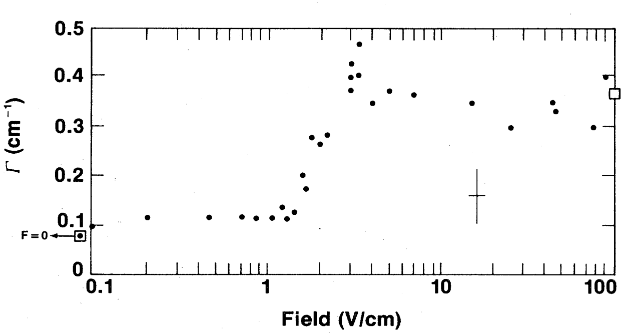

FIG. 4. Field dependence of the $J=5$ even-parity level at 49 836.0 cm^{-1}. Excitation is via the $J=2\rightarrow3\rightarrow4$ levels indicated in Fig. 1. The sudden increase in width occurs in the region where the Stark manifolds of adjacent underlying Rydberg levels overlap.

V/cm.[5] Thus one would expect field-induced ionization of the isolated even-parity level to become important at field strengths of about 23 V/cm, but not at lower field strengths. As shown above, however, in our odd-parity spectra we observed levels of Rydberg series in the region we have studied converging to the $^{10}D^{\circ}_{7/2}$ level which have principal quantum numbers between 55 and 70. They are perturbed by fields of a few V/cm. The fact that such Rydberg series exist in this spectral range provides the basis for the interpretation of the weak-field width dependence of the narrow even-parity resonance at 49 836 cm^{-1}.

The field dependence of the narrow even-parity resonance, our primary object of investigation, is shown in Fig. 4. The width stays constant up to a field strength of about 1 V/cm, and then increases rapidly until it reaches a new plateau of about four times larger width at a field strength of about 3 V/cm.

In zero field, the observed even-parity resonance is narrow because of its high angular momentum J. In the absence of a field, the configuration mixing with the nearby Rydberg levels is very small, and it can mix only with levels of the same J, which are also narrow. Autoionization, which is due to configuration interaction in the atomic core, scales roughly as l^{-5} (the centrifugal barrier hinders the high-l level from penetrating the core). An electric field F mixes the l levels of a high-n Rydberg level at very low fields. At $F\,(\text{a.u.}) \cong \frac{1}{3}n^5$, the Ingliss-Teller limit, adjacent n levels begin to overlap, and even the lowest-l levels, which in general have the largest quantum defects and the largest autoionization widths, become mixed with the other l levels. Thus for this field region and higher they form a virtual continuum of overlapping mixed-l states. Their widths are intermediate between the broader low-l states and the narrow high-l states.

In the above sense, the Ingliss-Teller limit corresponds not only to the onset of the n-mixing region, but to the full l-mixing region as well, at least for high-n Rydberg levels. Due to this strong l mixing (and thus J mixing) in fields beyond the Ingliss-Teller limit, virtually any of these Rydberg states can configuration mix with "isolated" states via the r_{12}^{-1} interaction including levels of high J. If the Rydberg levels are broader than the isolated level, this field-inducing mixing will result in the width of the isolated level increasing to a value comparable to that of the mixed Rydberg levels.

While the above model is a qualitative one, it does lead to two quantitative predictions consistent with our observations. The isolated $J=5$ level at 49 836 cm^{-1} broadens in the region 1.5—3.0 V/cm; the Ingliss-Teller limit for $n=63$ (see Fig. 2) is 1.7 V/cm. The field-induced width of the level is about 0.35 cm^{-1}, comparable to widths of the Rydberg perturber levels seen in Fig. 2(b).

In conclusion, we suggest that the width of narrow, high-angular-momentum, autoionizing levels can be significantly altered at electric fields near to or greater than $F\,(\text{a.u.}) = \frac{1}{3}n^5$ (the Ingliss-Teller limit), where n is the principal quantum number of nearby Rydberg levels. The presence of such Rydberg levels is a common situation for autoionizing levels of complex atoms like Gd, due to the high density of low-lying excited states of the ion.

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