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THE INTERACTION OF BLACKBODY RADIATION WITH XENON
RYDBERG ATOMS

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The Interaction of Blackbody Radiation with
Xenon Rydberg Atoms

by

George. Flavius Hildebrandt

A THESIS SUBMITTED
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and Astronomy

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Xenon Rydberg Atoms

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George Flavius Hildebrandt

Abstract

Effects due to the interaction between the 300K background blackbody radiation (BBR) and xenon nf Rydberg atoms are reported. Transitions to nearby d and g levels are observed and the transition rates are found to be consistent with the predictions of a simple theoretical calculation which makes use of electric dipole matrix elements obtained by use of the quantum defect method. When the radiation background is reduced to that appropriate to a black body at liquid nitrogen temperature by cooling the apparatus, the transition rates are also observed to decrease. The reduction in the transition rates to the d and g states is consistent with the calculated decrease in the ambient blackbody flux. The total net depopulation rate of the f states is reduced as well when the temperature of the environment is lowered. The change in the observed lifetimes of the f states is in good agreement with the calculated decrease in the blackbody-induced depopulation rate.

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CHAPTER I

Introduction

A. Brief Summary

Table I-1 summarizes some of the more salient features of atoms in highly excited ($n \gtrsim 10$) states. (The values in the table are derived from the hydrogen atom. In much of the discussion in this chapter, hydrogenic results will be used freely to describe general properties of Rydberg atoms, since the dominant potential or highly excited electron experiences is the coulombic attraction with the ion core.) The large geometric cross sections, small binding energies and long lifetimes of atoms in high Rydberg states combine to ensure that these atoms play an important role in a number of environments, both earth-bound⁽¹⁻³⁾ and extra-terrestrial.⁽⁴⁻⁶⁾ With the growing sophistication of laboratory production and detection techniques, Rydberg atoms have quickly evolved from astrophysical and laboratory curiosities to an entirely new and rapidly expanding field in atomic physics.

In the past few years extensive studies of Rydberg-molecule and Rydberg-atom collisions have been undertaken⁽⁷⁻²⁰⁾ using a variety of atomic Rydberg species. This effort has been paralleled by a great deal of theoretical investigation into the nature of collisions with highly excited atoms.⁽²¹⁻²⁷⁾

In many of the collisional experiments undertaken in this laboratory,⁽⁷⁻⁹⁾ a number of which were undertaken by the author, a persistent background signal was consistently observed for

Table I-1. Summary of important features of Rydberg atoms. Values listed are calculated for hydrogen.⁽⁴¹⁾ Both the functional n dependence and specific values for $n = 25$ and $n = 40$ are given.

		n = 25 $l = 3$		n = 40 $l = 3$	
f(n)					
MEAN ATOMIC RADIUS	n^2	500 Å		1300 Å	
GEOMETRIC CROSS SECTION	n^4	$7.7 \times 10^5 \text{ Å}^2$		$5.1 \times 10^6 \text{ Å}^2$	
TERM LEVELS	n^{-2}	22 meV		9 meV	
SEPARATION OF n LEVELS	n^{-3}	1.6 meV (13 cm ⁻¹)		0.4 meV (3 cm ⁻¹)	
LIFETIMES	n^3	15 μsec		70 μsec	

which no reasonable explanation was immediately forthcoming. In the tradition of Wilson and Penzias, the troublesome noise was thoroughly investigated, characterized and probed until an unexpected explanation emerged: the Rydberg atoms, in addition to their other unique properties, interact with surprising ease with the background black body radiation (BBR) that is present in the environment. The probability of a highly excited atom making a transition to another quantum state due to the absorption of a long wavelength BB photon is so large, in fact, that Rydberg atoms have been proposed as sensitive narrow bandwidths detectors of far infrared (FIR) radiation.⁽²⁸⁻³⁰⁾ The quantitative measurements which verified this conclusion form the basis of this thesis. The rest is history.

B. Production of Rydberg Atoms

Rydberg atoms were first produced in the laboratory by electron impact excitation⁽³¹⁻³³⁾ which produced, quite naturally, a broad mixture of excited atomic and ionic states. In order to produce in the laboratory Rydberg atoms in single well defined states, optical excitation was employed, using radiation first from continuum sources⁽³⁴⁾ and then from tunable dye lasers.⁽³⁵⁾

To achieve the large amount of energy required to excite an atom from the ground state to a state very close to the continuum, a variety of multi-step excitation techniques have evolved which basically involve the population of an intermediate state by either electron impact-⁽⁷⁾ or photo-

excitation,⁽¹⁰⁾ followed by optical excitation to the desired Rydberg state (see Fig. I-a). As has been described previously,⁽³⁶⁾ the technique employed in this laboratory for the production of xenon Rydberg atoms involves electron impact excitation to the 3P_0 metastable level followed by photo-excitation to a high-lying nf state.

C. Detection of Rydberg Atoms

The most widely used method for detecting highly excited atoms (and the method employed in this work) is field ionization. A useful starting point for understanding the phenomenon of field ionization is the classical view of an atom in an external electric field (Fig. I-b). If the potential energy, $-eEz$, due to the external field is superimposed on the $-e^2/r$ coulombic potential due to the residual ion core, the result is the appearance of a potential maximum, $V_{\max}$, on the "down-field" side of the atom. Classically, for electrons with term energies above the potential maximum, the electron will be able to move freely from the ion core and ionization will result. An electron with energy less than $V_{\max}$ will be unable to surmount the barrier and will remain bound to the core. As the field is increased, therefore, the atom will be stable against ionization until $V_{\max}$ is depressed below the term energy of the excited electron, at which point ionization immediately occurs.

The value of the critical field strength at which ionization occurs is a sensitive function of the state of excitation

I-a. Typical methods of producing high Rydberg atoms
in the laboratory.

Xe**

Na**

H**

I-b. Potential well as seen by a Rydberg electron: unperturbed coulombic potential ($E = 0$); with an external electric field applied ($E > 0$). Levels which are shifted up in energy by the Stark effect are drawn on the up-field side of the potential, indicating that their wave functions have minimum probability density close to the potential "hump." In three dimensions the local potential maximum over which the electron may escape is referred to as the saddle point.

of the atom, hence the usefulness of field ionization in identifying the quantum state of the Rydberg atom under study. Solving for $V_{\max}$ and setting it equal to the zero-field term energy of a Rydberg state yields the following zeroth-order expression for the critical field at which ionization occurs:

$$F_c \cong \frac{1}{16} n^{-4} \quad (\text{atomic units}) \quad (\text{I-1})$$

The critical field for a number of atomic systems has indeed been found to vary as n^{-4} . (36,37)

Things are never as simple as they seem, however, and it may seem strange at first that this simple result obtains. The full quantum mechanical picture of an atom in an electric field is indeed quite complicated, yet surprisingly enough, the final result of a quantum mechanical treatment of the field ionization of xenon Rydberg atoms does predict behavior similar to the classical model.

In the field ionization procedure relevant to the experiment, the atom is initially in a field-free environment. An external electric field is then applied to the atom at a rate of increase of $\sim 3 \text{ v cm}^{-1} \text{ nsec}^{-1}$ until the atom ionizes. How the atom gets from zero field to ionization is the subject of Fig. I-c. The figure is drawn for the $m_l = 0$ manifolds for $8 \leq n \leq 11$ of hydrogen, but it qualitatively represents the general features of field ionization of different atoms at higher values of n . As the field is increased from zero, the energy levels of the atom shift according to the Stark effect.

I-c. Intersecting $|m_\ell| = 0$ manifolds for hydrogen in an increasing electric field. The qualitative features evident in the field ionization of $n = 9$ hydrogen may be extended to higher n for other Rydberg atoms.

The Stark manifolds shown in the figure are calculated using fourth-order perturbations theory.⁽³⁸⁾ At the terminus of each Stark state a series of dots indicates a region of significant ionization probability, as estimated from a quantum mechanical calculation.⁽³⁹⁾ Field ionization rates are shown in the figure for $n = 11$. For all states shown, the dotted region begins at an ionization rate of 10^7 sec^{-1} and ends at 10^{11} sec^{-1} .

Also shown in Fig. I-c is the classical ionization threshold, F_c (see Eq. I-1). It is interesting to note that most of the states in the figure are relatively stable for a large range of field values for which their energies are sufficient to allow classical ionization.⁽⁴⁰⁾ This is due to the fact that the wave functions of these states have very little probability density in the vicinity of the saddle point⁽⁴¹⁾ (see Fig. I-b). The states which have the greatest probability density at the saddle point are the bottom states in each manifold, and these states actually do ionize close to the classical threshold. Those states with the least probability density at the saddle point ionize at the largest fields, furthest above the classical threshold. This result is strictly true only for a purely Coulombic potential. It has been pointed out⁽⁴⁰⁾ that non-Coulombic terms in the potential seen by electrons in alkali Rydberg atoms cause stable states of one n manifold to couple with unstable states of high-lying manifolds, resulting in a larger ionization rate of the otherwise stable states.

An atom will follow a particular path through the energy level diagram of Fig. I-c as the field is increased. The details of its path depend crucially on the atom's behavior in regions where Stark states of different manifolds approach one another. Non-Coulombic terms in the Hamiltonian of the atom dictate that states of the same $|m_\ell|$ will not cross.⁽⁴²⁾ (This is why only states with $m_\ell = 0$ are shown in Fig. I-c: manifolds of different $|m_\ell|$ do not interact with this picture at all.) How severely states of the same $|m_\ell|$ repel each other depends on the magnitude of the non-Coulombic terms in the Hamiltonian.⁽⁴⁰⁾

Two extreme types of behavior must be considered: diabatic and adiabatic passage to ionization. If the atom is in a state which does not interact strongly with other states (or if the time rate of change of the applied field is large enough) then the atom does not change its state as the field increases, and thus follows a path such as that indicated by the heavy line in Fig. I-c. All curve crossings are said to be traversed diabatically in this case, and the atom ultimately ionizes in the dotted region.

If, however, the atom is in a state which strongly interacts with other states of the same $|m_\ell|$ (or if the field is changing very slowly) then the atom will follow a path similar to the dashed lines in Fig. I-c. The atom avoids each crossing, and as a result successively changes its effective state as the field increases. This is referred to as adiabatic passage to ionization. The path continues until the atom makes a crossing

with a highly ionizing state from the lowest member of a higher-lying Stark manifold. When this crossing is approached, the atom assumes the character of this already unstable state and spontaneously ionizes. Recall that the classical ionization threshold coincides with the quantum mechanical threshold for ionization for the lowest members of each Stark manifold of a given $|m_\ell|$. Thus states that pass from zero to high electric fields adiabatically are expected to ionize near the classical threshold.

If all the states of the $n = 9$ manifold were to ionize adiabatically, the observed critical fields would fall in the appropriately marked range of fields in Fig. I-c which is centered around 50 kv/cm. If the states of the $n = 9$ manifold ionize diabatically, ionization would not be observed until about 75 kv/cm. The effect of strong intermanifold interactions is thus to compress the range of field values at which ionization occurs and to lower the average critical field for a particular manifold. This result can easily be visualized with reference to Fig. I-c, in that the states associated with the $n = 9$ manifold are trapped between the adiabatic extremes of the $n = 8$ and $n = 10$ manifolds.

The majority of ionization phenomena reported in the literature arises from adiabatic ionization. Recently, both adiabatic and diabatic ionization behavior have been reported for highly excited sodium.⁽⁴³⁾ The probability of diabatic passage for a given field slew rate increases as either n or $|m_\ell|$ increases.⁽⁴³⁾

The path to ionization taken by Xe(nf) is predominantly adiabatic, as can be shown from fairly general arguments. Figure I-d shows a field ionization spectrum of xenon 27f, which is observed to ionize around 700 v cm^{-1} . There are two possible paths to ionization, indicated in Fig. I-e. If the xenon atom follows a diabatic path to ionization (dashed line) then the energy of the state at ionization would be given by point B, which is clearly below the classical ionization threshold or saddle point line. On the other hand, if xenon 27f ionizes adiabatically (solid line), then the energy of the state at 700 v cm^{-1} would be given by point A, which occurs where ionization is energetically permissible. The adiabatic paths presented in the figure are not accurate representations of the actual path that the energy of an atomic state would take to ionization, but are merely meant to exemplify the adiabatic trapping of a xenon nf state between manifolds. Nevertheless it is evident that a diabatic path to ionization is not consistent with the data, while an adiabatic path is.

To see if xenon nf states exhibit any diabatic ionization behavior in addition to the demonstrably adiabatic behavior above a spectrum of 36f was taken in which the applied field attained values adequate to ionize any atom which might have taken a diabatic path to high fields. As Fig. I-e reveals, only a single adiabatic peak is observed. From this we conclude that xenon nf states ($|m_l| = 0, 1, 2, 3$) ionize adiabatically. This type of analysis is sufficient to interpret the field ionization spectra which will be presented in Chapter IV,

I-d. Field Ionization feature of xenon 27f.

I-e. The possible paths of xenon 27f to ionization via an increasing electric field are shown very schematically. Adiabatic paths are indicated by solid lines, diabatic paths by dashed lines. The saddle point line is also shown.

I-f. Single adiabatic ionization feature associated
with 36f.

and an exact knowledge of the precise path taken to ionization is not necessary.

In the next chapter many of the surprising ramifications of the interaction of BBR with xenon Rydberg atoms will be discussed. The quantum defect method, which is used to theoretically check the results of Chapter IV, is also outlined.

CHAPTER II

Interaction of Rydberg Atoms with BBR

Blackbody radiation (BBR), like poverty, is always with us, yet is seldom noticed. A glance at Fig. II-a explains why this is so. The scale on the left gives the energy density as a function of wavelength (solid line) while the scale on the right gives the magnitude of the electric field as a function of wavelength (dashed line) that is associated with ambient BBR at 300K. In most everyday situations these values would not cause very much excitement, especially in those wavelength regions which are the usual domain of the atomic physicist, the near infrared to the ultraviolet. The peak of the BB distribution does not occur until fairly far into the infrared, and even then the energy density of the radiation field would appear to be negligible for most atomic physics experiments.

Would be, that is, if it were not for the unique properties of Rydberg atoms. Most radiative transitions are well approximated as dipole transitions,⁽⁴⁴⁾ for which the transition probability from one state, γ , to another, γ' , is proportional to the product of the energy density of the radiation field and the square of the radial matrix element, $\int_0^\infty \rho_\gamma(r) r \rho_{\gamma'}(r) dr$, connecting the two states. As might be expected from the Rydberg atom's impressive size (Table I-1), the radial integrals coupling adjacent highly excited states are likewise gargantuan. Figure II-a shows the squared radial integral (using hydrogenic wave functions) for the transition

II-a. Blackbody energy flux density in watts cm^{-2}
 μ^{-1} (solid line) and associated rms electric
field intensity in volts $\text{cm}^{-1} \mu^{-1/2}$ (dashed line)
as a function of wavelength.

$nf \rightarrow (n-1)g$ for $6 \leq n \leq 28$. The increase of almost four orders of magnitude over the range of n covered in the figure is given greater significance by the fact that the Rydberg-Rydberg transitions are taking place in the far-infrared (FIR) portion of the spectrum where the BBR energy density is most appreciable. For reference, the wavelengths appropriate to the xenon Rydberg transitions which will be discussed in Chapter IV are given in Table II-1.

As mentioned in Chapter I, the effect that BBR has on Rydberg atoms was not appreciated until it was advanced as an explanation for troublesome background signals. Once the effect was recognized, however, a number of researchers hastened to verify the expected temperature dependence,^(45,46) and to identify and characterize the different phenomena that arise from BBR-Rydberg interactions.⁽⁴⁷⁻⁵²⁾ The first ramification that presents itself is the loss of purity of the single-state Rydberg population that the experimenter has striven to create. As has been mentioned numerous times before⁽⁵³⁻⁵⁴⁾ the laboratory study of highly excited atoms came into its own only after techniques had been developed to produce atomic populations of single, well-defined quantum states. Without this ability, most data analysis would rapidly prove to be intractable. It has been pointed out⁽⁵⁴⁻⁵⁵⁾ that spontaneous radiative decay presents no problem in this regard, for the vast majority of such transitions are to states of low principal quantum number. BB-induced transitions, however, are predominantly to states proximate in

Table II-1. Wavelengths of Rydberg-Rydberg transitions observed in this experiment. Figure III-d shows the amount of radiation available at these wavelengths. Transitions are from the parent n_f state (left column) to n'_g and n''_d states.

nf	n'g	$\lambda_{f \rightarrow g}$ (μm)	n"d	$\lambda_{f \rightarrow d}$ (μm)
20	21	370	23	588
	22	204	24	247
	23	146	25	164
24	25	632	27	1009
	26	344	28	420
	27	245	29	276
25	26	713	28	1139
	27	387	29	428
	28	275	30	311

$$\text{II-b. } \left| \int_0^{\infty} f_{nf}(r) f_{(n-1)g}(r) r^2 dr \right|^2 \text{ for hydrogen.}$$

energy to the initial state, as can clearly be seen in Fig. II-c. If the total BB depopulation rate from a given state is comparable to or larger than the spontaneous decay rate, then the initially pure Rydberg state population will quickly degenerate into an unseemly mash of different states, each with about the same lifetime, collisional ionization rate, etc. as the state the experimenter is trying to characterize.

To intelligently discuss the seriousness of this problem it is useful to separate out the spontaneous and BB depopulation mechanisms. The probability of an atom making a transition from one state to another by the absorption of a BB photon is frequently expressed as ⁽⁵⁶⁾

$$B_{n \rightarrow n'} \rho(\bar{\nu}) \quad (\text{sec}^{-1}) \quad (\text{II-1})$$

where $B_{n \rightarrow n'}$ is the Einstein B coefficient connecting states n and n' and where $\rho(\bar{\nu})$ is the energy density per unit wave number of BBR at the transition wave number $\bar{\nu}$, which is expressed as ⁽⁵⁷⁾

$$\rho(\nu) = 8\pi h c \bar{\nu}^{-3} (e^{hc\bar{\nu}/kT} - 1)^{-1} \quad (\text{II-2})$$

But the Einstein B coefficient is related to the Einstein A coefficient by the well-known formula ⁽⁵⁶⁾

$$B_{n \rightarrow n'} = \frac{1}{8\pi h c \bar{\nu}^{-3}} A_{n \rightarrow n'} \quad (\text{II-3})$$

so the transition probability from state n to state n' due to the ambient BB flux is simply

II-c. Transition rates associated with blackbody-induced photoexcitation and photo-de-excitation of Xe(20f) to neighboring g states.

$$A_{n \rightarrow n'} (e^{hc\bar{\nu}/kT} - 1)^{-1} \equiv A_{n \rightarrow n'} \bar{n}(\bar{\nu}) \text{ (sec}^{-1}\text{)} \quad (\text{II-4})$$

where $\bar{n}(\bar{\nu})$ is the photon occupation number⁽⁵⁷⁾ at the wave number $\bar{\nu}$.

The sum of all possible spontaneous and stimulated transitions from initial state n is thus expressed as

$$\begin{aligned} \frac{1}{\tau_n} &= \sum_{n' < n} A_{n \rightarrow n'} + \sum_{n' \neq n} \bar{n}(\bar{\nu}_{n \rightarrow n'}) A_{n \rightarrow n'} \\ &\equiv \frac{1}{\tau_n^s} + \frac{1}{\tau_n^{BB}} \end{aligned} \quad (\text{II-5})$$

where τ_n is the total "apparent" lifetime of state, τ_n^s is the lifetime against spontaneous transitions of state n , and τ_n^{BB} is the lifetime against all BB transitions, explicitly including those to the continuum states.

Cooke and Gallagher⁽⁵⁰⁾ have derived an approximate expression for the second summation in II-5:

$$\frac{1}{\tau_n^{BB}} \approx 6.8 \times 10^4 (T/n^2) \text{ sec}^{-1} \quad (\text{II-6})$$

where T is the temperature in degrees Kelvin and n is the effective principal quantum number of state γ . This equation overestimates the BB depopulation rate, but becomes more accurate as n^* and ℓ (the angular momentum of state γ) increase. As ℓ increases, the spontaneous lifetime τ_r^n increases, so that the BB depopulation rate eventually dominates. For $n = 25$, $\ell = 24$ the spontaneous decay lifetime is ~ 880 μsec .⁽⁵⁸⁾ From Eq. II-6, however, the lifetime against all

BB transitions is only $\sim 30 \mu\text{sec}$. Hence, in only $6 \mu\text{sec}$, an originally pure $n = 25$, $l = 24$ state has lost over 20% of its initial population to neighboring long-lived Rydberg states. This is but an extreme example of an effect which must be accounted for even in states of low l .

It is also immediately obvious from Eqs. II-5 and II-6 that the total "apparent" lifetime of a Rydberg state depends on the intensity of the radiation field it experiences (see Chapter IV). Experiments which require an accurate knowledge of the lifetimes of highly excited atoms may be subject to error if the FIR spectrum that the atoms are exposed to is not constant.

The lifetime of a Rydberg atom may be affected by BBR in another, more exotic way. In Rydberg populations of $\sim 10^3$ atoms, masing action has actually been observed, and populations of only $\sim 10^5$ atoms have exhibited superradiance.⁽⁵²⁾ The effect was revealed by the enhanced net transition rate from the laser-excited state to the nearest state with a lower term energy (i.e., the transition with the highest gain and lowest threshold). The masing and superradiant action were both triggered by BBR and not spontaneous emission. Hence a sufficiently dense Rydberg population may serve as a BBR amplifier, resulting in even greater sensitivity in the detection of FIR photons.^(51,52,59) The effects of stimulated emission are unobservable in the present experiment.

Another aspect of BBR that has not been considered until recently^(48,50) is the effect of the oscillating electric field

that is associated with the ambient radiation field (see Fig. II-a). The rapidly varying electric field shifts the Rydberg levels relative to the ground state of the atom according to the "a.c." Stark effect.⁽⁶⁰⁾ For highly excited atoms in a BBR field appropriate to 300K, an approximate shift of ~ 2 kHz, independent of n or l , has been calculated.⁽⁵⁰⁾ In addition to the electric field, there is a corresponding magnetic field of sufficient strength ($\sim .01$ gauss at $200 \mu\text{m}$) to cause a shift of the atomic hyperfine frequencies of cesium that is only slightly smaller than the precision of current frequency standards.⁽⁶¹⁾

Although BBR gives rise to a number of surprising and unusual effects, this thesis is concerned with one particular aspect, namely the redistribution of excited states that occurs as a result of photoexcitation and photo-de-excitation of Rydberg atoms in a BBR field. In order to fully elucidate this process, it is necessary to measure the BB-induced transition rates from one Rydberg state to another and confirm these results by comparing them to a theoretical model. The calculated transition rates are obtained by use of the quantum defect method, which is discussed in the next section.

B. Theoretical Calculations

As was outlined in Section A of this chapter, the problem of calculating the transition probability of an atom from state γJ to state $\gamma' J'$ reduces to evaluating the A coefficient, which is given as⁽⁶²⁾

$$A_{\gamma J \rightarrow \gamma' J'} = \frac{4\omega^3}{\hbar c^3} \frac{e^2}{(2J+1)} \sum_{mm'} |\langle \gamma J m_J | T_{1q} | \gamma' J' m_J' \rangle|^2 \quad (\text{II-6})$$

where T_{1q} is the tensor operator whose components are the spherical components of a vector $\vec{r}$. Thus⁽⁶³⁾

$$T_{10} = z \quad ; \quad T_{1\pm 1} = \mp \frac{1}{\sqrt{2}} (x \pm iy) \quad (\text{II-7})$$

or, more simply

$$T_{1q} = \left(\frac{4}{3} \pi\right)^{\frac{1}{2}} r Y_{1q} \quad (\text{II-8})$$

where the Y_{1q} are the familiar spherical harmonics.

The excited states of xenon are describable by the j - ℓ coupling notation.⁽³⁶⁾ In this coupling scheme, approximate wave functions are obtained by coupling the orbital angular momentum, ℓ , of the running electron to the total angular momentum, j , of the core. The resulting angular momentum is designated as K , to which is then coupled the spin angular momentum, S , of the excited electron to give a total angular momentum J . The wave functions in Eq. (II-6) are expressed as $|j\ell KSJm_J\rangle$, and are described by the quantum numbers j , ℓ , K , S , J and m_J . These wave functions are formed by summing the products of wave functions which are described by the quantum numbers j , m_j , ℓ , m_ℓ , S and m_s .⁽⁶⁴⁾ By use of the Wigner-Eckart theorem⁽⁶⁵⁾ and the appropriate vector coupling coefficients⁽⁶³⁾ it can be shown that⁽⁶⁴⁾

$$\begin{aligned}
|\langle j m_J | T_{1q} | \gamma' J' m_J' \rangle|^2 &\equiv |\langle j \ell K S j m_J | T_{1q} | j' \ell' K' S' J' m_J' \rangle|^2 \\
&= (2J+1) (2J'+1) (2K+1) (2K'+1) \delta(j, j') \\
&\quad \times \begin{pmatrix} J & J' & 1 \\ -m_J & m_J' & q \end{pmatrix}^2 \begin{Bmatrix} J & J' & 1 \\ K' & K & S \end{Bmatrix}^2 \begin{Bmatrix} \ell' & K' & j' \\ K & \ell & 1 \end{Bmatrix}^2 \\
&\quad \times |\langle \ell || T_1 || \ell' \rangle|^2 \tag{II-9}
\end{aligned}$$

where the quantity in parentheses is a 3-j symbol, the quantities in brackets are 6-j symbols, and the last factor is the reduced matrix element of the operator T_{1q} .⁽⁶⁵⁾ From Eq. (II-8) it can also be shown that⁽⁶⁶⁾

$$|\langle \ell || T_1 || \ell' \rangle|^2 = (2\ell+1) (2\ell'+1) \begin{pmatrix} \ell & 1 & \ell' \\ 0 & 0 & 0 \end{pmatrix}^2 \left| \int_0^\infty f_\ell(r) r f_{\ell'}(r) dr \right|^2 \tag{II-10}$$

where $f_\ell(r)$ is the radial wave function of the running electron multiplied by r .

Substituting Eqs. (II-9) and II-10) into (II-6) and summing over all orientations, we have finally

$$\begin{aligned}
A_{\gamma J \rightarrow \gamma' J'} &= \frac{4\omega^3 e^2}{3\hbar c^3} \delta(j, j') (2J'+1) (2K+1) (2K'+1) \\
&\quad \times (2\ell+1) (2\ell'+1) \begin{pmatrix} \ell & 1 & \ell' \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{Bmatrix} J & J' & 1 \\ K' & K & S_1 \end{Bmatrix}^2 \\
&\quad \times \begin{Bmatrix} \ell' & K' & j' \\ K & \ell & 1 \end{Bmatrix}^2 \left| \int_0^\infty f_\ell(r) r f_{\ell'}(r) dr \right|^2 \\
&\equiv \frac{4\omega^3 e^2}{\hbar c^3} \delta(j, j') C_{\gamma J \rightarrow \gamma' J'} \left| \int_0^\infty f_\ell(r) r f_{\ell'}(r) dr \right|^2 \tag{II-11}
\end{aligned}$$

The angular factors ($C_{\gamma J \rightarrow \gamma' J'}$) in front of the radial integral in Eq. (II-11) may be evaluated in a straightforward fashion from tables provided in the literature. (63,67)

In the j - l coupling scheme, excited states are designated as $(2S_c^{+1})_{L_{cj}} n l [K]_J$, where S_c and L_c are, respectively, the spin and orbital angular momentum quantum numbers of the core, n is the principal quantum number of the excited electron, and j , l , K and J have their usual meaning. In xenon, two core configurations are possible: $2P_{1/2}$ and $2P_{3/2}$. If the core is in the $2P_{1/2}$ state, the n quantum number is usually primed. The states that are excited in the present experiment (36) are of the $(2P_{3/2})nf[3/2]_1$ series, where $20 \leq n \leq 29$. The d and g states which are optically accessible from the nf state may be determined by applying the usual j - l selection rules ($\Delta j = 0$; $\Delta K = 0, \pm 1$; $\Delta J = 0, \pm 1, 0 \nrightarrow 0$). The allowed $f \rightarrow d$ and $f \rightarrow g$ transitions together with the corresponding angular factors calculated from II-11 are shown in Table II-2.

The radial integral in Eq. (II-11) may be calculated by use of the well-known quantum defect method first proposed by Bates and Damgaard. (68) In the central field model the radial wave functions $f_i(r)$ and $f_f(r)$ satisfy a differential equation of the form (in atomic units)

$$\frac{d^2 f}{dr^2} + (2V - \frac{l(l+1)}{r^2} - E) f = 0 \quad (\text{II-12})$$

where V is the potential the electron moves in, l is the usual angular momentum quantum number, and E is the energy parameter.

Table II-2. Angular factors ($C_{\gamma \rightarrow \gamma'}$ in Eq. (II-11))
for allowed $f \rightarrow d$ and $f \rightarrow g$ transitions for
an atom described in the $j-l$ coupling
scheme.

parent f state	allowed d,g state	C_{rot}
$f [3/2]_1$	$g [5/2]_2$	$4/7$
	$d [1/2]_0$	$1/5$
	$d [1/2]_1$	$1/10$
	$d [3/2]_1$	$1/10$
	$d [3/2]_2$	$1/50$
	$d [5/2]_2$	$3/350$

It has been shown⁽⁶⁸⁾ that the potential V closely approximates its asymptotic form in that region of r which gives the dominant contribution to the radial integral $\int_0^\infty f_i(r) f_f(r) r dr$. Thus the wave functions f_i and f_f need only be accurate for large and moderate values of r . In this region, it is sufficient to approximate V by its asymptotic form, Z/r , Z being the excess charge on the core. The differential equation (II-12) thus becomes (setting $Z = 1$)

$$\frac{d^2 f}{dr^2} + \left(\frac{2}{r} - \frac{l(l+1)}{r^2} - E \right) f = 0 \quad (\text{II-13})$$

the solutions of which must satisfy the boundary conditions $f \rightarrow 0$ as $r \rightarrow \infty$. The solution to Eq. (II-13) is

$$f_{n^*l}(r) = C_{n^*l} e^{-r/n^*} f^{n^*} \sum_{\alpha=0}^{\infty} a_{\alpha}^{n^*l} r^{-\alpha} \quad (\text{II-14})$$

with

$$a_0 = 1 \quad ; \quad a_{\alpha} = a_{\alpha-1} \left(\frac{n^*}{2\alpha} \right) [l(l+1) - (n^*-\alpha)(n^*-\alpha+1)] \quad (\text{II-15})$$

where $n^* = E^{-1/2}$. The normalization factor C_{n^*l} is determined by requiring that $\int_0^\infty (f_{n^*l}(r))^2 dr = 1$. In the calculations performed for this thesis, the normalization constants were calculated numerically. Note that if n^* is an integer, the series in Eq. (II-14) terminates at $\alpha = n^* - l - 1$, and $f_{n^*l}(r)$ is then equal to the exact hydrogenic eigenfunction.

The integral in Eq. (II-11) can then be expressed as

$$\int_0^\infty f_{n^*l}(r) f_{n^{*'}l'} r dr = C_{n^*l} C_{n^{*'}l'} \sum_{\substack{\alpha=0 \\ B=0}}^{\infty} a_{\alpha}^{n^*l} a_B^{n^{*'}l'} \int_0^\infty e^{-r(\frac{1}{n^*} + \frac{1}{n^{*'}})} r^{n^*+n^{*'}+1-\alpha-B} dr \quad (\text{II-16})$$

The integral in II-16 may be integrated trivially⁽⁶⁹⁾ to obtain the result

$$\int_0^{\infty} f_{n^*,l}(r) f_{n^{*'},l'}(r) dr =$$

$$C_{n^*,l} C_{n^{*'},l'} \sum_{\substack{\alpha=0 \\ B=0}} a_{\alpha}^{n^*,l} a_B^{n^{*'},l'} \left(\frac{1}{n^*} + \frac{1}{n^{*'}} \right)^{-(n^*+n^{*'}+2-\alpha-B)}$$

$$\times \Gamma(n^* + n^{*'} + 2 - \alpha - B) \quad (\text{II-17})$$

In evaluating Eq. (II-17) a criterion must be established for terminating the series. Bates and Damgaard originally proposed neglecting all terms in II-17 for which $\alpha < n^* - l$; $B < n^{*'} - l'$.⁽⁷⁰⁾ This is tantamount to ignoring small powers of r in the integrals of II-16. The main contribution from these terms comes from the region close to the origin, where the true potential differs significantly from the Coulomb potential assumed in this derivation. In calculating the radial matrix elements between highly excited states, this cut criterion was found to provide excellent agreement with experimentally measured values (see Table IV-1). The integral was found to be largely insensitive to small deviations of the maximum summation indices, α_0 and B_0 . The calculated radial integrals were also checked for stability against small changes in the value of the lower limit of integration. If the large majority of contribution to the integration does indeed come from regions where r is large, then the result should be essentially constant if the lower limit of integration is varied between 0 and some small finite value of r , r_c . (To evaluate the radial

integral with a nonzero lower limit is trivial: the gamma function $\Gamma(a)$ in (II-17) is merely replaced by an incomplete gamma function $\Gamma(r_c; a)$. The radial integrals coupling highly excited states were found to vary $\lesssim 1\%$ for $0 \leq r_c \leq 3.0$ (a.u.).

Uncertainty in the cutoff criterion and contribution from regions of small r result in $\sim 2\%$ uncertainty in the calculated radial matrix elements connecting high Rydberg states. The amount of error associated with the choice of the effective principal quantum numbers, n^* and $n^{*'} in (II-17) is not known. In quantum defect theory, the energy parameter E and the associated effective quantum number, $n^* \equiv n - \delta_{n\ell}$, where $\delta_{n\ell}$ is the quantum defect of the n, ℓ state, are introduced as empirical parameters to be determined by direct measurement. The quantum defects used in this work were obtained from tabulated values of atomic energy levels found in the literature.⁽⁷¹⁾ The range of n for which energy levels have been accurately measured in xenon terminates at $n \cong 13$. In order to project the measured quantum defects to the region of n where the present experiment is conducted ($20 \leq n \leq 29$) it is desirable to fit the tabulated data to a Ritz formula.⁽⁷²⁾ Unfortunately, the quantum defects of xenon are not smoothly varying functions of n , and are not suitable for extrapolation, as can be seen from Fig. II-d. Instead of attempting an extrapolation to higher n , the quantum defects of the relevant states in xenon are estimated by averaging the quantum defects of the highest five levels available in the tabulated data for$

II-d. Quantum defects derived from Moore's ⁽⁷¹⁾
tabulation of atomic energy levels. The axis
on the left corresponds to the $nd [1/2]_0$ levels
(solid circles) while the axis on the right
corresponds to the $nd [1/2]_1$ levels (open circles).

each $n\ell[K]_J$ series. The averaged quantum defects for those nf and nd levels which were listed in Table II-2 are shown in Table II-3. No data are available on the quantum defects of g states in xenon. Since the g states are even less penetrating than the f states ($\delta_f \sim .056$) the quantum defect associated with the g series is assumed to be zero for the purpose of this calculation.

The radial matrix elements were not found to be critically sensitive to the value of the quantum defects chosen for the calculation. Variations in the quantum defects of the f and d series of $\sim 2-3\%$ resulted in a shift of $\sim 8-9\%$ in the radial integral. If the quantum defect of the g series was assumed to be $.001$ instead of zero, a change in the integral of $\sim 3\%$ was observed.

Recently, Edmonds et al. ⁽⁷³⁾ have published a semi-empirical formula that describes the behavior of the radial matrix element between two quantum defect wave functions as a function of n^* , ℓ , $n^{*'}$ and ℓ' . Using the data in reference (73) one may compute the radial matrix element between any two states whose effective principal quantum numbers, n^* and $n^{*'}$, differ by 4 or less. The results of our calculation agree very well with the values obtained from the data of Edmonds et al.

The quantum defect method may also be extended beyond single-transition calculations to provide information about the decay of Rydberg atoms. If it were possible to calculate each transition rate contained in Eq. (II-5), one would be

Table II-3. Averaged quantum defects (using tabulated data of Moore⁽⁷¹⁾) for the f, d and g states involved in the transitions listed in Table II-2.

State (1[K] J)	δ
$f [3/2]_1$	.056
$g [5/2]_2$	0
$d [1/2]_0$	2.54
$d [1/2]_1$	2.49
$d [3/2]_1$	2.16
$d [3/2]_2$	2.46
$d [5/2]_2$	2.41

able to arrive at a value for τ_n , the total lifetime of the Rydberg state. Let us once again consider separately the two terms given in (II-5); τ_n^S and τ_n^{BB} .

Given the agreement between calculated and observed BB-induced transition rates between neighboring Rydberg states, one would expect to be able to calculate τ_n^{BB} with a fair degree of confidence (refer once again to Fig. II-c). Direct calculation of radial matrix elements cannot be performed for wave functions whose principal quantum number is very large, however. The wave functions obtained from our computer program are probably reliable only up to $n \sim 35$. If the principal quantum number of the initial state is in the range $20 \leq n \leq 29$, then the major contribution to τ_n^{BB} is directly calculable, but the BB transition rates to states with $n \gtrsim 35$ must be estimated by a straightforward extrapolation technique. The extrapolated portion of the BB depopulation rate, $1/\tau_n^{BB}$, is ~ 8 -11% of the total BB rate.

We have so far only taken into consideration bound-bound transitions. Quantum defect theory has been applied to photoionization by a number of authors.⁽⁷⁴⁻⁷⁶⁾ The photoionization cross section is proportional to the square of the radial matrix element connecting the bound and continuum states. The free electron wave function has the asymptotic form⁽⁷⁶⁾

$$G_{k\ell}(r) \underset{r \rightarrow \infty}{\sim} k^{-\frac{1}{2}} \sin[x + \pi\delta_\ell(\epsilon)] \quad (\text{II-18})$$

with

$$x = kr - \frac{1}{2} \ell \pi + \frac{1}{k} \ln(2kr) + \arg \Gamma(\ell+1 - \frac{i}{k}) \quad (\text{II-19})$$

where $\epsilon = k^2$ is the energy of the ejected electron and where $\delta_\ell(\epsilon)$ is the quantum defect of the ℓ series extrapolated into the continuum. Since the bound state wave function of a Rydberg electron has many nodes, it is important to determine the phase of the continuum state wave function. From (II-18), it is obvious that the phase depends in part on the quantum defect, $\delta_\ell(\epsilon)$, of the positive-energy continuum state, which is obtained from an extrapolation of the bound-state δ_ℓ 's found in the literature. As was pointed out before, however, this procedure is not possible for xenon, due to the anomalous behavior of the observed quantum defects. Nonetheless, the depopulation rate due to photoionization may be estimated from the hydrogenic photoionization cross sections published by Burgess.⁽⁷⁷⁾ Integrating the product of the photoionization cross section $\sigma(\lambda)$ and the BB photon number density $n(\lambda;T)$ over all wavelengths and multiplying by c gives the equivalent total photoionization rate. From Burgess' data, a rate of $\sim 1.4 \times 10^3 \text{ sec}^{-1}$ is derived for hydrogen 20f, which is to be compared with a calculated BB depopulation rate for all bound-bound transitions of $3.3 \times 10^4 \text{ sec}^{-1}$. Hence photoionization contributes $\lesssim 5\%$ to $1/\tau_n^{\text{BB}}$.

The effects of BB and spontaneous depopulation cannot be separated for constant temperature. If the BB photon density is changed, however, only $1/\tau_n^{\text{BB}}$ changes while $1/\tau_n^{\text{S}}$ remains constant. If the total depopulation rate, $1/\tau_n$, is measured

at two different temperatures, the difference between them will simply be the difference in $1/\tau_n^{BB}$. The correlation of $\Delta(1/\tau_n)$ and $\Delta(1/\tau_n^{BB})$ provides a check on the above calculation. As will be shown in Chapter IV, the agreement between the calculated and observed effect of temperature on Rydberg state lifetimes is gratifying.

The quantum defect method may also be used to calculate τ_n^S . The spontaneous decay rate, however, is dominated by transitions to the low-lying excited states. This is due to the ω^3 factor in $A_{\gamma \rightarrow \gamma}$, which becomes very large for transitions to states of low principal quantum number. A greater proportion of the wave functions of these low-lying states lies within that region of r for which the potential deviates significantly from its asymptotic form. Nonetheless, the major contribution to the radial integral should come from regions of moderate to large r . Indeed, for simple systems the coulomb approximation appears to give quite satisfactory results for transitions involving low-lying excited states.^(68,72) Xenon is quite complicated, however, in that states of the same parity corresponding to different core configurations may interact.⁽³⁶⁾ As has been noted by many authors,^(55,36,78) the conventional $j\ell$ coupling scheme is not entirely satisfactory for describing the excited states of rare gas atoms.

The calculated and observed lifetimes for two xenon nf states are shown in Table II-4. Assuming that the τ_n^{BB} calculation is the more reliable, there appears to be about a

Table II-4. Observed lifetimes for Xe(20f) and Xe(25f) are compared with theoretically calculated lifetimes (including BB depopulation) obtained from the quantum defect method. The calculated values of τ_n^s are in only 20% agreement with those of Latimer,⁽⁵⁵⁾ a discrepancy which is probably due to the use of different series termination criterion.

nf	$\tau_{nf}^{\text{obs.}}$ (μsec)	$\tau_{nf}^{\text{calc.}}$ (μsec)
20	4.2	5.7
25	7.2	10.5

Error of observed lifetimes is 15%

35% discrepancy in the calculated and (indirectly) observed values for τ_n^S . Taking everything into consideration, even this agreement is probably fortuitous.

Calculation of τ_n^S requires more care in the use of the quantum defect method that was necessary for τ_n^{BB} . It is observed from the calculations that the first neglected term in the series in Eq. (II-17) is not necessarily small if the previous cut criterion is employed. For transitions to low-lying excited states the termination criterion of Bebb⁽⁷⁹⁾ is used. As expected, the radial integrals involving states of low principal quantum number are more sensitive to the value of r_c . The total spontaneous decay rate, $1/\tau_n^S$, varied by as much as 27% when r_c was adjusted between the values of 0 and 2.5 (a.u.). (The radius of maximum charge density for the outermost orbital (5_p) in the core has been calculated⁽⁸⁰⁾ to be 1.9 a.u.)

Despite the lack of earth-shaking success in obtaining theoretical agreement with observed lifetimes for xenon nf states, the quantum defect method was pushed to the limit once more in an attempt to calculate the lifetimes of highly excited nd and ng states. Xenon d and g states are populated via BB photoexcitation of f states. The lifetimes of the f states may be measured directly using standard techniques, but the lifetimes of the secondary d and g states may not be measured separately, for reasons which will become apparent in Chapter IV. To theoretically describe the time development of the BB populations observed in this experiment, some knowledge of

these lifetimes is necessary. Measured lifetimes for low-lying excited states of xenon are available in the literature⁽⁷⁸⁾ but the differences in the values that I have found are often considerable.⁽⁷⁸⁾ Extrapolation of these data obtained for states with $5 \leq n \leq 9$ to states with $20 \leq n \leq 30$ could easily result in lifetimes in error by a factor of 2 or greater. Similarly, there are no available calculations of lifetimes for xenon d and g Rydberg states, although an extensive tabulation of theoretical lifetimes for states of low principal quantum number is extant.⁽⁷⁸⁾ However, the agreement between theory and experiment is often unsatisfactory.

It was in order to fill this appalling gap in human knowledge that the calculation was attempted. The calculation of the g-state lifetimes is straightforward, as there is only one g substate that is populated by the BB transition (refer to Table II-2), which subsequently decays to five possible $nf[K]_J$ states and one $nh[7/2]_3$ state, as shown in Table II-5. The decay of the d levels is more complex as each of the five $nd[K]_J$ levels which are populated by BBR are indistinguishable in the experiment for a given n. In fact, only the aggregate lifetime of the five $nd[K]_J$ levels and the $(n-2)_g [3/2]_1$ level is measured in the experiment, as will be explained in Chapter IV. Thus the total lifetime of a particular nd state is arrived at by first calculating the total depopulation rates for each of the $nd[K]_J$ levels, multiplying these values by the appropriate fractional parentage

Table II-5. Angular factors ($C_{\gamma \rightarrow \gamma'}$) for the allowed $g \rightarrow f$ and $g \rightarrow h$ transitions, along with the tabulated quantum defects (in parentheses) for the appropriate f levels. The quantum defects for the g and h levels are assumed to be zero.

BB g state	allowed f,h states	$C_{\gamma \rightarrow \gamma'}$
$g[5/2]_2$	$f[3/2]_1$ (.056)	12/35
	$f[3/2]_2$ (.054)	4/105
	$f[5/2]_2$ (.031)	2/35
	$f[5/2]_3$ (.034)	1/245
	$f[7/2]_3$ (.021)	1/441
	$h[7/2]_3$	5/9

coefficients (i.e., the relative transition probabilities from the original f state), summing these rates and inverting. The allowed $d \rightarrow p$ and $d \rightarrow f$ transitions are listed for each of the five $nd[K]_J$ levels in Tables II-6 through II-10, along with the appropriate quantum defects and angular factors.

Transitions to the ground state ($J = 0$) are allowed for those d states with $J = 1$. The angular coefficients are worked out for this case in the literature.⁽⁶⁶⁾ Even though the quantum defect wave function is not expected to accurately represent the ground state of xenon, the technique is employed here in order to obtain a zeroth-order value for τ_{nd} .

Not surprisingly, the d -state lifetimes are sensitive to the choice of termination criterion and to the lower limit of integration, which probably means they are unreliable. The g -state lifetimes are fairly stable with respect to the choice of α_0 , B_0 and r_c ; the addition or subtraction of one extra term in the summation II-17 result in a change of $\lesssim 5\%$ in $1/\tau_{ng}$, and varying r_c from 0 to 3.0 (a.u.) resulted in a change of $\lesssim 8\%$ in $1/\tau_{ng}$. (The lifetimes include the effects of BBR, but the total depopulation rate is dominated by the spontaneous decay rate.)

The g -state lifetimes may be more reliable than the d -state lifetimes, but it is not possible to check them independently. The theoretical lifetimes may be compared with experiment only insofar as they are capable of reproducing the time development of a single BB feature, which is itself composed of a combination of d and g states. This will be attempted in Chapter IV.

Table II-6. Angular factors for the allowed $d[\frac{1}{2}]_0 \rightarrow p[K]_J$ and $f[K]_J$ transitions, including quantum defects (in parentheses) for the appropriate states. The fraction of the BB-excited d state that is due to $d[\frac{1}{2}]_0$ is .467.

BB d state	allowed p,f states	$C_{\gamma \rightarrow \gamma'}$
$d [1/2]_0$ (2.54)	$p [1/2]_1$ (3.60)	1/3
	$p [3/2]_1$ (3.53)	1/15
	$f [3/2]_1$ (.056)	3/5

Table II-7. Angular factors for the allowed $d[\frac{1}{2}]_1 \rightarrow p[K]_J$ and $f[K]_J$ transitions, including quantum defects (in parentheses) for the appropriate p, d and f states. The fraction of the BB-excited d state that is due to $d[\frac{1}{2}]_1$ is .233. The angular coefficient for transitions to the ground state is 2/81.

BB d state	allowed p,f states	$\theta_{\gamma \rightarrow \gamma'}$
$d [1/2]_1$ (2.49)	$p [1/2]_0$ (3.44)	1/9
	$p [1/2]_1$ (3.60)	2/9
	$p [3/2]_1$ (3.53)	1/90
	$p [3/2]_2$ (3.51)	1/18
	$f [3/2]_1$ (.056)	1/10
	$f [3/2]_2$ (.054)	1/2

Table II-8. Angular factors for the allowed
 $d[3/2]_2 \rightarrow p[K]_J$ and $f[K]_J$ transitions,
including defects (in parentheses)
for the appropriate p, d and f states.
The fraction of the BB-excited d state
that is due to $d[3/2]_2$ is .047.

BB d state	allowed p,f states	$C_{\gamma \rightarrow \gamma'}$
d $[3/2]_2$ (2.46)	p $[1/2]_1$ (3.60)	1/6
	p $[3/2]_1$ (3.53)	8/375
	p $[3/2]_2$ (3.51)	24/125
	p $[5/2]_2$ (3.57)	1/750
	p $[5/2]_3$ (3.55)	7/375
	f $[3/2]_1$ (.056)	3/250
	f $[3/2]_2$ (.054)	27/250
	f $[5/2]_2$ (.031)	4/125
	f $[5/2]_3$ (.034)	56/125

Table II-9. Angular factors for the allowed $d[3/2]_1 \rightarrow p[K]_J$ and $f[K]_J$ transitions, including quantum defects (in parentheses) for the appropriate states. The fraction of the BB-excited d state that is composed of $d[3/2]_1$ is .233. The angular coefficient for transitions to the ground state is 2/81.

BB d state	allowed p,f states	$C_{\gamma \rightarrow \gamma'}$
d $[3/2]_1$ (2.16)	p $[1/2]_0$ (3.44)	1/9
	p $[1/2]_1$ (3.60)	1/18
	p $[3/2]_1$ (3.53)	8/45
	p $[3/2]_2$ (3.51)	8/225
	p $[5/2]_2$ (3.57)	1/50
	f $[3/2]_1$ (.056)	1/10
	f $[3/2]_2$ (.054)	1/50
	f $[5/2]_2$ (.031)	12/25

Table II-10. Angular factors for the allowed $d[5/2]_2 \rightarrow p[K]_J$ and $f[K]_J$ transitions, including quantum defects (in parentheses) for the appropriate states. The fraction of the BB-excited d state that is composed of $d[5/2]_2$ is .020.

BB d state	allowed p,f states	$C_{\gamma \rightarrow \gamma'}$
d $[5/2]_2$ (2.41)	p $[3/2]_1$ (3.53)	63/250
	p $[3/2]_2$ (3.51)	7/250
	p $[5/2]_2$ (3.57)	14/125
	p $[5/2]_3$	1/125 .
	f $[3/2]_1$ (.056)	3/1750
	f $[3/2]_2$ (.054)	3/5250
	f $[5/2]_2$ (.031)	256/2625
	f $[5/2]_3$ (.034)	128/18375
	f $[7/2]_3$ (.021)	24/49

CHAPTER III

Experiment

A. General Apparatus

This chapter describes in detail the experimental apparatus used to undertake the program of research outlined at the end of the last chapter. Much has already been written (9,36,54) about the vacuum apparatus itself and the details of xenon Rydberg production and detection techniques which have been developed in this laboratory. I will not, therefore, belabor these subjects, but will rather devote most of my efforts to a description of the cold box and ancillary paraphenalia, as this hardware is unique to this experiment.

A general schematic of the apparatus is shown in Figure IIIa. As has been the case for some time now, a beam of neutral, ground state xenon atoms is formed by effusion through a multichannel glass array. A fraction of the beam is excited to the 3P_0 metastable level by electron impact excitation. The beam is then intersected at right angles by the output of a pulsed tunable dye laser. A small number (typically $\sim 1-5$ per laser shot) of atoms in the 3P_0 metastable state are then photoexcited to high-lying nf states. For this experiment, n is in the range $20 \leq n \leq 29$. The remainder of the metastable beam impacts on a surface detector which is used to monitor beam stability.

The dye laser cavity used for this experiment is slightly different from those which have been previously discussed, and is shown in Figure IIIb. The design is originally due to

III-a. General schematic of the apparatus.

III-b. Basic design of the Littman laser cavity
used in this experiment.

Littman^(81,82), and was adopted for its high output power and narrow linewidth. This cavity is also capable of producing a spectrally pure beam with very little untuned fluorescence, although care must be taken to properly align the focusing lenses. The amount of untuned radiation in the beam may be estimated by blocking the return beam from the tuning mirror, and comparing the output power with the power that is measured when lasing is allowed to occur. Typically a fluorescence to laser power ratio of .05 or less is sufficient.

The Rydberg atoms are created in a region bounded by two parallel fine copper wire mesh grids. Immediately after laser fire, the Rydberg atoms begin to interact with the ambient BBR, and the purity of the single-state Rydberg population is destroyed. During this time both grids are maintained at ground potential to ensure field-free conditions. To obtain information about the distribution of states as a function of time after laser fire, a selective field ionization (SFI) technique is used^(7,8). The mechanics of this technique are outlined in Figure IIIc. After a variable delay, a large negative voltage ramp is applied to the bottom grid while the top grid is held at ground potential. The resulting increasing electric field between the grids ionizes the xenon Rydberg atoms. The resulting free electrons are accelerated by the force of the electric field to a Johnston focused-mesh particle multiplier. The output of the multiplier is amplified and fed into the "stop" input of a multi-channel

III-c. General outline of selective field ionization technique used in this experiment.

analyzer (MCA). The "start" input of the MCA is synchronized with the start of the voltage ramp.

Once the MCA registers a pulse at the "stop" input, it is inactive for the remainder of the voltage ramp, and any pulses which arrive after the first one will not be recorded. Electrons which arrive soon after the ramp starts thus prevent the detection of electrons which arrive later. The experimental conditions are therefore arranged such that the probability of detecting an electron during any given laser shot is very low, typically $< .1$. In this circumstance an accurate representation of the electron arrival time distribution is obtained.

Atoms in different states will ionize at different voltages, and hence at different times on the voltage ramp. From the electron arrival time distribution obtained from the MCA, and from a knowledge of the temporal characteristics of the voltage ramp, a state map of the Rydberg atoms may be obtained for any arbitrary time after laser fire.

The voltage ramp increases from (0v.) to a maximum voltage, $V_{\max}$, in a characteristic risetime, t_R (see Figure IIIc). Typical values of t_R are in the range $300 \text{ ns} \leq t_R \leq 1200 \text{ ns}$. The slope of the ramp as a function of time is not constant, but for most of the SFI spectra presented in Chapter IV, the slew rate (dV/dt) of the ramp is approximately 1 v/ns .

A LeCroy model No. 3001 MCA is used for this experiment. The full memory of 1024 channels may be divided into four quarters of 256 channels each. The time interval during

which the MCA is active may be adjusted from 100 to 1000 ns by selecting one of four precision resistors. The active time interval remains constant whether the MCA is operated in the full- or quarter-memory mode. For the majority of data reported here, the quarter-memory mode is employed. This means that each channel of memory corresponds to a time interval of from .4 to 4 ns.

B. The Cold Box

When faced with the task of changing the ambient flux of long wavelength radiation in a vacuum apparatus, two basic alternatives present themselves: heating or cooling the environment. If a small enclosed metal structure is placed around the interaction region (defined by the intersection of the xenon and laser beams), it is an easy task to elevate its temperature substantially via resistive heating, provided it is thermally isolated from the rest of the apparatus. There are, however, practical limitations to the maximum temperature that can be achieved. Even though the multiplier may not be physically attached to the structure, it must "see" the interaction region to be able to detect charged particles. Since it will, therefore, communicate radiatively with the heated object, its temperature will increase, thereby increasing its dark current and degrading its detection characteristics⁽⁸³⁾. Outgassing rates are also increased at elevated temperatures, thus increasing background count rates.

Taking these factors into account, the maximum temperature that can conveniently be applied in the apparatus is about 500K. As can be seen from Figure IIIId, the BB photon density in the long wavelength region ($\gtrsim 100 \mu\text{m}$) increases only by about 70% in going from 300K to 500K. This is not as large an effect as is desired.

A variant of this approach was also considered. It is possible to obtain calibrated filaments whose spectral emissivities are known⁽⁸⁴⁾. If such a filament is placed near the interaction region and heated, an extremely high effective photon temperature may be produced for the immediate environment of the Rydberg atoms, without having to physically heat a massive object. Unfortunately, these filaments are not very well characterized in the FIR region^(85,86).

While increasing the photon density appears to be of questionable value, decreasing it presents many attractive aspects. From Figure IIIId, it can be seen that in going from 300K to 78K (the boiling point of nitrogen) the long wavelength radiation density decreases almost by a factor of four, so that the expected change in the BB signal is more easily measured. Moreover, if the region is cooled, spurious BB-induced processes are suppressed, thus providing a more favorable signal to noise ratio for other experiments. For these reasons I elected to reduce the temperature of the region surrounding the Rydberg atoms in order to positively demonstrate the effect of BB radiation on Rydberg atoms.

III-d. Blackbody photon flux density as a function
of temperature and wavelength.

To this end, a copper box, shown in Figure IIIe, was constructed and placed in the vacuum. The xenon and laser beams enter and exit through small holes in the side, as shown. The fine mesh grids are mounted in the box, and bound the interaction region. Charged particles created in the interaction region pass through the mesh and exit the box through a small aperture at the top.

As was mentioned before, the top grid of the interaction region is held at ground potential while the voltage ramp is applied to the bottom grid. Since the box itself is grounded, the region between the top grid and the exit aperture is essentially field-free (except for penetration fields), and charged particles drift through this region with whatever energy is imparted to them in the interaction region. Once through the exit aperture, the charged particles come under the influence of the voltages applied to the accelerating grids of the multiplier housing (grids 1-4 in Figure IIIe), and are attracted to the first dynode of the multiplier. Typically, +300 volts is applied to the multiplier first dynode in order to detect electrons. The multiplier housing is physically separate from the box and is not cooled.

The box itself is of cylindrical geometry, and is about 20 cm tall and 10 cm across the diameter (note the scale size in Figure IIIe). The box is roughly divided into a bottom half, where the cooling actually takes place, and a top half which houses the grids.

III-e. Copper box and electron multiplier housing.
Grids 1 and 2 are maintained at high positive potential while grids 3 and 4 are grounded. The voltage ramp is applied to grid 5. For simplicity, the grid support structures inside the box shown without O-rings and retaining clamps.

The bottom half of the box is a solid copper cylinder around which are wrapped several turns of a single, continuous $3/16$ " o.d. copper tube. The tube is silver-soldered onto the box to provide good thermal contact. The bottom plate of the box (which is silver-soldered onto the lower half-cylinder) has a 1" diameter hole in the center of it to provide increased pumping speed out of the box. A circular copper platform which completely covers the pumping orifice is mounted on 1" high copper legs over the bottom plate. The interaction region is thus shielded from direct view of the large aperture in the bottom plate. Mounted directly underneath the shielding platform is a 400 watt commercial projector bulb (not shown), so that the temperature of the box may be elevated if so desired. The bulb heater was employed to bake the box when it was initially placed in the apparatus, but, for reasons stated above, was not found useful for the BB experiment itself. A $1/2$ " wide, $1/4$ " thick copper flange is silver-soldered onto the bottom half-cylinder to ensure an adequate heat flow to the rest of the box.

The top half of the box consists of a number of stacked copper rings which are firmly attached to the flange of the lower half by eight $1/4$ -20 bolts (not shown). The stacked geometry allows for a variety of possible grid configurations, but for the present experiment, only two grids (those enclosing the interaction region) are used. Up to four grids may be installed in the box. The thickness of the rings

varies from 1/8" (grid retaining rings) to 3/8" (spacer rings). A single ring, with appropriately dimensioned slots milled into it, provide the necessary apertures for the entrance and egress of the metastable and laser beams. There are 16 rings in all. A copper plate covers the top of the box and is also tightly bolted to the rest of the assembly. A small aperture in the top plate allows charged particles out of the box.

The grids are formed by stretching Buckbee-Mears 100 lines per inch, 78% transmissive, fine copper mesh across a light, rigid stainless steel frame, shown in Figure IIIf. The mesh is both stretched and held in place by the frictional pull of a viton O-ring, which is in turn secured by a metal retaining ring. In the assembly process, a pre-sized piece of mesh is laid across the circular protrusion of the grid frame. The O-ring is then positioned over the protrusion and placed on the mesh. The metal retaining ring is then used to apply even pressure on the O-ring, so that it is forced over the outer edge of the extension, pulling the mesh down with it. The outer edge of the protrusion is beveled so that the mesh does not tear during this operation. As the O-ring slides down, the mesh is stretched uniformly in all directions. When the retaining ring is pushed below the top of the protrusion, it is secured to the grid frame with 12 1-56 screws. If the mesh is not torn, the end result is a circular mesh grid surface $2\frac{1}{2}$ " in diameter, which is flat to within .001".

III-f. Assembly of fine wire copper mesh grids.

This is a cross-sectional view of the
circular support rings.

Since stray magnetic fields might bend the trajectory of an electron to the extent that it would impact on the top plate rather than exit through the aperture, care must be taken to eliminate any magnetic materials from the immediate vicinity of the interaction region. Accordingly, only non-magnetic 304 stainless steel is used in constructing the grid assemblies, and no spot-welding is necessary. A commercial gaussmeter verifies that the structure produces a magnetic field of not more than 30 milligauss.

The outer edge of the circular grid frame is clamped in between two copper retaining rings, as shown in Figure IIIe. The grid structure is electrically insulated from the grounded box by thin circular strips of teflon which separate the copper rings from the grid frame. The teflon is thin enough to provide adequate thermal conductivity from the box to the grid, yet thick enough to stand off at least 2500 v. The surfaces of the two mesh grids are ~ 3 mm apart.

The height of the metastable beam must obviously be less than this separation to avoid scattering from the grid wires. To define the dimensions of the xenon beam, an aperture 3.5 mm wide by 1.9 mm high is mounted on the box in front of the metastable entrance aperture. The beam defining aperture is maintained at ground potential due to its contact with the box. Mounted directly in front of it is a larger orifice which is electrically isolated from the box. Metastable xenon atoms pass through the first aperture and either pass through the beam defining aperture or hit the aperture plate.

If a metastable atom strikes a metal surface, there exists a certain probability, γ , that it will eject a secondary electron from the metal surface. Electrons ejected from the aperture plate may be attracted to the multiplier as a result of the positive potential on the first dynode and produce a large (~ 100 kHz) continuous background count rate. To suppress this unwanted signal, a positive potential of about 30 volts is applied to the first aperture plate to attract secondary electrons ejected from the surface of the beam defining aperture plate.

Copper-constantan thermocouples are attached to the side and top of the copper box, and to the bottom grid. A commercial thermocouple meter, calibrated for copper-constantan, is used to measure temperatures down to about 80K. When liquid nitrogen is flowed through the cooling tube, about 3/4 of an hour is required for the three thermocouple leads to reach equilibrium at cryogenic temperatures.

The entire box assembly is supported by four 8-32 threaded rods, which are bolted to the bottom plate of the box. The support rods are in turn attached to a teflon platform, which is then bolted to the floor of the vacuum chamber. The box is thus thermally isolated from the environment except for the long cooling tube.

This means, however, that the box has a fairly high impedance electrical ground as well. When large voltages are applied to the bottom grid in sub-microsecond intervals, the box, which is capacitatively coupled to the grid,

experiences fairly large (~ 1 v.) long duration voltage oscillations. These oscillations are in turn picked up by the multiplier and counted. To suppress this ringing, a low inductance brass strip is used to ground the box to the metal floor of the apparatus. In situ measurements with a Tektronix 465 oscilloscope verify that the voltage waveform on the bottom grid corresponds to the output of the ramp generator (to within 100 mv) and that excursions of the potentials of the top grid and box from ground are minimal (less than 50 mv).

The presence of the low inductance ground creates an unwanted heat path from the box to the apparatus. Because of this, a constant flow of liquid nitrogen is necessary if the temperature of the box is to be maintained at 80K. As this is not always possible, the average temperature of the box is generally 80-90K during data acquisition.

The average photon density inside the box is different from that which would be appropriate for a black body cavity at the temperature of the box. This is because room temperature radiation leaks in through the various necessary orifices in the box. An exact knowledge of the photon density inside the box is difficult to obtain since the reflectivity of the interior of the box is nonzero. Bare copper, in fact, has a reflectivity very close to unity for wavelengths in the FIR. For an uncoated box, therefore, a photon entering by one of the holes would undergo very many reflections before

being absorbed. In that case, the photon density inside the box would be very nearly the same as outside.

Fortunately, a precise knowledge of the absorptivity of the interior of the box is not necessary in order to obtain a reasonable estimate of the photon density. Simple equilibrium considerations yield the following relation:

$$\frac{\text{in}_{\text{BB}\rho}^T}{\text{out}_{\text{BB}\rho}^T} = \frac{R_A + a}{R_A} \quad (\text{III-1})$$

where $\frac{\text{in}_{\text{BB}\rho}^T}{\text{out}_{\text{BB}\rho}^T}$ is the ratio of the photon density inside the box to the photon density of a BB cavity at temperature T, $\frac{\text{out}_{\text{BB}\rho}^T}{\text{out}_{\text{BB}\rho}^T}$ is the ratio of the photon density outside the box to the photon density of a BB cavity at temperature T, R_A is the ratio of the area of the holes to the effective absorber area in the box, a is the absorptivity of the absorber, and T is the temperature of the box.

$\frac{\text{in}_{\text{BB}\rho}^T}{\text{out}_{\text{BB}\rho}^T}$ is plotted as a function of a in Figure IIIg. A family of curves is generated by varying R_A . $\frac{\text{out}_{\text{BB}\rho}^T}{\text{out}_{\text{BB}\rho}^T}$ is assumed to be 3.75, which is the ratio of photon densities at 1000 μm for a BB at 300K and a BB at 80K. Thus, if a is zero, $\frac{\text{out}_{\text{BB}\rho}^T}{\text{out}_{\text{BB}\rho}^T} = \frac{\text{in}_{\text{BB}\rho}^T}{\text{out}_{\text{BB}\rho}^T}$, as expected. As can be seen from the figure, an increase in the absorptance from .7 to 1 changes the photon density by only a few percent. The photon density is also not critically dependent on the hole area to absorber area ratio as long as it is small (a change in the ratio of areas from .05 to .15 changes the photon density by less than 25%).

III-g. Ratio of photon density inside the box to the photon density appropriate to a blackbody cavity at the temperature of the box (vertical axis) as a function of the absorbtivity of the walls of the box for different ratios of hole area to absorber area (see Eq. (III-1)).

In order to provide for adequate reduction of FIR radiation, commercial copper wool is attached to the inside of the copper box and coated with carbon soot. The wool structure provides for a large number of internal reflections, resulting in the effective trapping and absorption of long wavelength photons. A water vapor laser, emitting two strong lines at 311 and 331 μm , was used to examine the absorptivity of the wool in the FIR region, and values of $> 90\%$ were obtained at these wavelengths. Enough wool was attached to the interior of the box to establish a hole area to absorber area ratio of $.15 \pm .05$.

Once the average photon density inside the box has been established, it is necessary to account for the effect of the direct first-pass radiation from the holes which the Rydberg atoms experience. The box is as large as can conveniently be fit into the apparatus so as to minimize the solid angle of the outside environment to which the Rydberg atoms are exposed. If the box is cooled to 80K and the photon density outside the box is assumed to be that of a BB cavity at 300K, it can easily be shown from a simple solid angle calculation that the amount of radiation at the center of the box due to first-pass leakage through the holes is less than 10% of the total radiation density that the Rydberg atoms experience in the FIR.

Of perhaps greater concern is the radiation which enters the box through the metastable input aperture which is due to the electron gun in the metastable source. A

tungsten wire is resistively heated to about 2300K to produce an electron current of about 10 ma. The interaction region in the box has a direct view of the hot wire. Fortunately, the wire is both very far from the box (~ 1 meter) and very small (.025" diameter). It can again be shown from solid angle considerations that the percentage of radiation in the FIR region which the Rydberg atoms are exposed to which is due to the hot filament is negligible ($< 5\%$).

This calculation assumes that the wire is the only object in the apparatus with an effective photon temperature in the FIR of 2300K. Since the reflection coefficient for bare metal in the FIR is almost one, however, it may be the case that metal surfaces in the apparatus that are between the hot filament and the interaction region also have an effective photon temperature for long wavelength radiation much larger than 300K. To ensure that the photon density inside the apparatus is that appropriate to a BB at 300K, sooted copper wool is attached to the interior wall of a vacuum chamber intermediate between the interaction region and the metastable source. The intermediate chamber communicates with the interaction region and the metastable source via small apertures. To demonstrate that the hot tungsten wire is not a problem, an auxiliary wire is placed in the metastable beamline inside the intermediate chamber. The secondary filament can be heated to 2300K and above without affecting metastable production. No increase in the

BB-produced photoexcitation signal is observed as the test filament is heated.

In the next chapter, the nature of the photoexcitation signals will be discussed in detail.

CHAPTER IV

Discussion of Results

A. Introduction to Xenon BB SFI Spectra

In Chapter I the theory of field ionization of Rydberg atoms is discussed in terms of the behavior of an atomic level in an increasing electric field. In Chapter III the mechanics of a selective field ionization (SFI) technique is outlined by which the characteristic ionizing voltage of a Rydberg state may be determined. In this chapter the SFI spectra of xenon Rydberg states which result from BB induced transitions are presented and interpreted in light of the concepts developed in Chapter I. The SFI technique is employed to determine the population of BB populated Rydberg states as a function of time after laser fire and environmental temperature. The results of these investigations are then compared with theoretical calculations.

A typical xenon SFI spectrum is shown in Figure IV-a. A single pure state, 27f, is represented by a single peak with a maximum occurring around 700 v/cm. The spectrum is taken shortly after laser fire, before significant redistribution of Xe(27f) atoms into neighboring Rydberg states can occur. As is shown in Chapter I, xenon Rydberg nf states exhibit no discernible diabatic ionization behavior of $n \lesssim 40$, hence the voltage ramp in Figure IV-a is not increased beyond that which is necessary to ensure complete adiabatic ionization of 27f. As the ramp approaches $V_{\max}$, dV/dt decreases (note the voltage scale at the bottom of the figure). Hence the peak in IV-a is broader than the one in I-d.

IV-a. SFI spectrum of Xe(27f) shortly after laser
fire.

The spectrum in Figure IV-b is taken using the same voltage ramp as in IV-a, after a delay of several microseconds. Photo-excitation of the laser produced 27f state by BBR results in the population of d and g states whose term energies are higher than the term energy of 27f. These states ionize at lower voltages than does 27f, and hence appear as a series of peaks to the left of the main peak which is due to the original f state.

The composition of these peaks may be deduced from the known structure of xenon. Figure IV-c depicts a highly generalized schematic representation of the paths that xenon d, f and g states take in an increasing electric field, assuming totally adiabatic behavior. The ordering of the energy levels at zero field is accomplished by use of the quantum defects for xenon d, f and g states which were given in Chapter II. As the field is increased, the 27f state is Stark shifted downward in energy until it starts to interact with the upward-shifted levels of the $n = 26$ manifold. The 27f state successively changes its effective Stark state as the field increases until it makes a crossing with an already highly ionizing state near the classical ionization threshold. The average trajectory of the original 27f state from low fields to ionizing fields is depicted by the heavy line terminating at point A.

The states closest in energy at zero field to 27f which are accessed by BB-induced transitions are 27g and 29d. However, as can be seen from the figure, these states are likewise adiabatically trapped between the $n = 26$ and $n = 27$ manifolds,

IV-b. SFI spectrum obtained after allowing Xe(27f) to interact with background 300K radiation for 6 μ sec. The BB peaks to the left of the main peak are identified by their constituent d and g states.

IV-c. Interpretation of BB-populated SFI features. An adiabatic passage to ionization of a parent nf state is schematically illustrated by the solid line A. When the path crosses the classical ionization threshold (B) the state ionizes at point 1. The BB-excited $(n+1)g$ and $(n+3)d$ states follow the paths labeled C and D respectively as the field increases. Both paths cross the classical ionization threshold near point 2, and thus ionize at essentially the same electric field. The first peak that appears on the low-field side of the parent nf peak thus results from the adiabatic ionization of xenon atoms in $(n+1)g$ and $(n+3)d$ states, the second peak from atoms in $(n+2)g$ and $(n+4)d$ states, and so forth.

and thus also cross the classical ionization threshold at point A. The voltages at which 27f, 27g and 29d appear to ionize are essentially equal, and cannot be resolved using this technique. In general, ng and $(n+2)d$ will contribute to the nf peak for any time t after the laser pulse that is greater than zero. This contribution is very small ($< 10\%$) if t is less than $\sim 3-4$ lifetimes of the nf state, and is neglected. To avoid ambiguity, therefore, the SFI feature that occurs at the characteristic ionizing voltage of the nf state is referred to as the "laser-produced nf peak" even though this nomenclature is strictly applicable only at $t = 0$.

Also shown in Figure IV-c are the BB-populated states 28g and 30d. These states are adiabatically trapped between the $n = 27$ and $n = 28$ manifolds, and hence follow paths which are crudely approximated by the pair of heavy lines which terminate at point B. These two states together comprise the ionization feature immediately to the left of the 27f peak in Figure IV-b, and are referred to collectively as the "first BB peak." The "second BB peak" thus consists of 29g and 31d, and so forth.

It is evident from Figure IV-c that the position of the first BB peak should correspond to the critical field of 28f, that the second BB peak should appear where 29f would, and so on. This prediction is easily confirmed by keeping the ramp fixed and tuning the laser to successively higher nf states. In general, then, the BB-populated $(n+i)g$ and $(n+i+2)d$ states form the i^{th} BB peak which appears at the same field strength as would $(n+i) f$.

The preceding interpretation of the peaks which appear in Figure IV-b is predicated on the assumption that xenon d and g states follow predominantly adiabatic paths to ionization. This cannot be positively verified experimentally (as was done for f states) because xenon n'd and n" g states are only created indirectly from parent nf states. If the secondary d and g states were indeed ionizing diabatically, one would expect to observe signal at larger field strengths than the (adiabatic) critical field of the primary f state. Some ionization is observed in this region, but no more than can be plausibly explained by the spontaneous and stimulated decay of the parent f state to lower-lying d and g states which subsequently ionize adiabatically (see Chapter IV, section D for a discussion of stimulated emission data).

Nonetheless, it may be inferred from fairly straightforward arguments that the vast majority of atoms in d and g states pursue adiabatic paths to ionization. Recall that the probability of diabatic passage for a given slew rate decreases as $|m_l|$ decreases. Thus if f states (with values of $|m_l| = 0, 1, 2, 3$) ionize adiabatically, d states (with $|m_l| = 0, 1, 2$) must also ionize adiabatically. The $|m_l| = 4$ component of xenon g states may, however, exhibit diabatic ionization tendencies. Yet, even if the $|m_l| = 4$ component were to completely ionize diabatically, 9/10, or 90%, of the BB-populated g state would ionize diabatically. (87)

B. Time Dependence of Photoexcitation Signal

Once the structure of the BB photoexcitation signal is understood, the transition rates from xenon nf states to $n'd$ and $n''g$ states may be measured by observing the time dependence of the BB signal. This is done by taking spectra similar to IV-b for different delay times after laser fire.

The time dependence of the first three BB peaks which evolve from a parent $25f$ state is shown in Figures IV-d through IV-f. The circles are experimental values, while the solid curves are the result of an empirical fit through the data. (The fitting procedure is described in detail in section C of this chapter.) The dashed curve in Figure IV-d gives the population of the $25f$ state as a function of time for comparison. The ordinate axes are normalized to unit Rydberg production (of $25f$) at $t = 0$.

The experimental method by which these data are taken is conceptually straightforward. A series of BB spectra are taken at various times after laser fire under identical conditions of laser power, metastable beam density and Rydberg production rate. In practice, however, this is a difficult and tedious undertaking. Each spectrum requires $1-2 \times 10^5$ laser shots to ensure sufficient statistics in the BB peaks. At a laser repetition rate of 30 Hz, this translates into 1-2 hours of data accumulation for each of the thirteen points in Figures IV-d,e,f. It is a formidable task to ensure adequate stability of experimental conditions over the time required to measure one point, to say nothing of the time required to measure

IV-d. Time development of the BB feature comprised of Xe(26g) and Xe(28d) states populated by transitions from Xe(25f). The time axis refers to the interval between the laser pulse and the time at which ionization occurs. The ordinate axis is normalized to unit Rydberg production at $t = 0$. The dashed curve shows the decay of the parent 25f state.

IV-e. Time development of the BB features comprised of Xe(27g) and Xe(29d) states populated by transitions from Xe(25f).

IV-f. Time development of the BB feature comprised of Xe(28g) and Xe(30d) states populated by transitions from Xe(25f).

thirteen points. Short term (~ 1 hour) stability problems are dominated by fluctuations in laser wavelength. Large time scale (~ 10 hours) instabilities are generally traceable to a slow decay of nitrogen laser power and metastable beam intensity, and to long term degradation of laser dye, which results in a worsening of the fluorescence to laser power ratio.

To mitigate these difficulties the following data taking procedure is adopted. The MCA is operated in the "quarter-memory" mode (see Chapter III) with each quarter-memory devoted to a single BB spectrum at a particular time after the laser pulse. The spectra are taken concurrently in order to average out the effects of short-term drift. Only one quarter-memory may be accumulating data at any one time, however, so it is necessary to alternate between them. Assume that X laser shots are required for each spectrum in order to obtain sufficient statistics in the BB peaks. To initiate the procedure, the ramp is delayed for t_1 μ sec after laser fire, and the first quarter-memory is activated for X/N laser shots, where $N \sim 10$. The time delay for the ramp is then adjusted to t_2 μ sec, the second quarter-memory is activated for X/N laser shots, and so forth. After the fourth quarter-memory has been allowed to accumulate data for X/N laser shots, the procedure starts over again with the first quarter. The cycle is repeated N times until each of the four spectra represent X laser pulses worth of data. A block of data, referred to as A , is thus acquired for times t_1 , t_2 , t_3 and t_4 .

Additional blocks of data must be taken if more than four times are desired. Although each block of data is taken under a consistent, stable set of conditions, experimental parameters will of course vary from block to block. In order to normalize one block to another a common time, t_b , is reserved as a benchmark for comparison. For example, a second block of data, block B, would then be taken at times t_4 , t_5 , t_6 and t_7 . The size of the peaks in the spectra taken at time t_4 are used to normalize block A to block B. This procedure may be repeated for any desired number of blocks (in the case of Figures IV-d through IV-f, four blocks were used).

It is useful to normalize the data thus obtained to unit Rydberg production of the parent nf state at $t = 0$. To do this, the total nf population is measured at a time, t_c , which is typically about one radiative lifetime after laser fire. In this circumstance the main peak is diminished to the extent that the probability per laser pulse of registering an ionization event at any point on the ramp is less than .1 and the MCA dead-time problem discussed in Chapter III is largely alleviated. (In order to enhance the BB peaks the experimental conditions are such that, for times close to laser fire, the probability of detecting an atom in the parent nf state is $\gtrsim .5$.) The residual effect of the MCA dead-time may be eliminated by a small correction which is applied iteratively to each point. The correction is discussed in detail in Appendix A.

The end result is an accurate profile of the parent nf state at some calibration time, t_c . The profile is then integrated to yield the total nf population at t_c , $N_o(t = t_c)$. From a knowledge of the apparent lifetime of the nf state, this immediately yields $N_o(t = 0)$. The normalized, integrated BB peaks are then divided by this number to provide the final result shown in Figs. IV-d,e,f. This entire procedure is outlined graphically in Fig. IV-g.

The time axes in Figs. IV-d through f are assigned according to when the i^{th} BB peak actually ionizes. This is determined by keeping the voltage ramp fixed and tuning the laser to excite the $(25+i)$ f state, which ionizes at the same voltage as the i^{th} BB peak. The amplified output of the multiplier is displayed on a Tektronix model 465 oscilloscope, which is triggered by the output of an ultraviolet-sensitive photodiode which is used to detect the output of the nitrogen laser. The difference between the start of the oscilloscope sweep and the appearance of the multiplier pulse gives the time interval between laser fire and the ionization of the $(25+i)$ f state, in addition to various time delays which must be taken into account. These delays are associated with electron flight time (~ 10 ns), transit time in the electron multiplier (~ 30 ns), cables (~ 15 ns), and amplifiers and associated electronics (~ 45 ns).

The error bars in the magnitude of the BB peaks are due to statistics (7%), background subtraction (12%), block to block normalization (10%) and normalization to unit Rydberg production at zero time (14%) to produce a net uncertainty of $\sim 23\%$ in the

IV-g. Outline of data taking procedure used to obtain time development of BB features. In upper left portion of figure three separate unnormalized blocks of data are shown. The data points at common times are used to normalize the blocks of data to each other, as shown in the upper right portion of the figure. Finally, the parent peak-BB peak ratio at one particular time is used (along with the measured lifetime of the parent state) to define the scale of the ordinate axis.

case of the first BB peak. The calculated error is somewhat larger for the other BB peaks which are smaller and less well defined than the first. The uncertainty associated with the time of ionization is due to electronic jitter in the variable delay pulses which is used to start the voltage ramp.

There are three main sources of background signal which must be taken account of: continuous production of spurious electrons by collision of xenon metastable atoms with background gas molecules or metal surfaces, direct production of unwanted nf states by untuned laser fluorescence, and overlap between neighboring BB or parent nf peaks. The first background is easily determined for each channel by measuring the constant count rate observed with the multiplier ungated and multiplying by the total time each channel is active. The effect of laser fluorescence on a BB spectrum may be ascertained by tuning the laser in between two adjacent nf states and taking a SFI spectrum under similar conditions of laser power and metastable beam density. The amount of overlap between adjacent peaks is estimated by use of a straightforward graphical technique. Because the first BB peak is adjacent to the large main peak, there is a large uncertainty in the size of the overlap background signal to subtract at small t . This is reflected in the size of the error bars in Fig. IV-d at early times.

C. Model of Time Dependent Photoexcitation Signal

To completely describe the time dependent behavior of a BB-excited Rydberg state one would have to account for a variety of population mechanisms, such as transitions from the parent nf state to the BB-induced state and transitions from other BB-populated states, as well as de-population mechanisms, namely BB-induced and spontaneous transitions to other states. Then, to fully characterize a single BB peak, the dynamics of each of the constituent states would have to be solved independently. This procedure would require an infinite set of coupled differential equations as well as knowledge of an infinite set of transition rates. Fortunately, such an impossibly complicated program is not necessary in order to adequately describe the data in Figs. IV-d-f, as the solid lines indicate. These lines are obtained from a much more tractable modeling procedure which is arrived at by a series of simplifying assumptions, which are now described.

To begin with, the population mechanisms of a BB state may, to good approximation, be narrowed down to transitions from the parent nf state. As can be seen graphically in Fig. IV-d, the size of the laser excited nf peak is much larger than any of the BB-excited peaks (note the scales of Figs. IV-e-f) for several lifetimes of the nf state (the lifetime of 25f is $7.2 \mu\text{sec}$). It is thus reasonable to neglect, for small t ($0 \leq t \lesssim 3 \tau_{\text{nf}}$), second-order population channels which involve transitions from BB-excited states.

The depopulation of both the parent nf state and BB-excited states may be characterized by an "apparent" lifetime which includes the effects of spontaneous and BB-induced transitions. Thus,

$$\frac{1}{\tau_{\gamma}} = \frac{1}{\tau_{\gamma}^n} + \frac{1}{\tau_{\gamma}^{BB}} \quad (IV-1)$$

where τ_{γ} is the apparent lifetime of state γ , τ_{γ}^n is the natural (BBR-free) lifetime, and τ_{γ}^{BB} is the lifetime against BB-induced transitions.

The time dependent behavior of the parent nf state is thus described by the equation

$$\frac{dN_o}{dt} = - \frac{N_o}{\tau_o} \quad (IV-2)$$

again neglecting second-order effects such as repopulation from BB states.

A full description of the growth and decay of the i^{th} BB peak would seem to require four independent parameters; two transition rates from the parent nf state to the n'g and n"d states comprising the peak, and two lifetimes governing the decay of the d and g states. In general, however, an adequate fit through the data is obtained by assuming that the time development of the BB peak is described by a single transition rate from the parent nf state and a single aggregate lifetime. Thus the differential equation governing the i^{th} BB peak is simply

$$\begin{aligned}
\frac{dN_i}{dt} &= -\frac{N_i}{\tau_i} + B_{O \rightarrow i} \rho(\nu) N_O \\
&\equiv -\frac{N_i}{\tau_i} + \frac{N_O}{\tau_{O \rightarrow i}^*}
\end{aligned}
\tag{IV-3}$$

where τ_i is the lifetime of the i^{th} BB peak, $B_{O \rightarrow i}$ is the Einstein B coefficient, $\rho(\nu)$ is the BB photon density at the appropriate frequency ν , and $1/\tau_{O \rightarrow i}^*$ is the total transition rate, in inverse seconds, from the nf state to the n'g and n"d states which constitute the i^{th} BB peak. Thus

$$\frac{1}{\tau_{O \rightarrow i}^*} = \frac{1}{\tau_{nf \rightarrow n'g}^*} + \frac{1}{\tau_{nf \rightarrow n"d}^*} .
\tag{IV-4}$$

Assuming that $N_O(t = 0)$ is some nonzero, finite value and that $N_i(t = 0)$ is zero, Eqs. IV-2 and IV-3 have the straightforward solutions

$$N_O(t) = N_O(0) e^{-t/\tau_O}
\tag{IV-5}$$

and

$$N_i(t) = N_O(0) e^{-t/\tau_O} \frac{1/\tau_{O \rightarrow i}^*}{1/\tau_i - 1/\tau_O} [1 - e^{(1/\tau_O - 1/\tau_i)t}]
\tag{IV-6}$$

The apparent lifetime of the parent nf state, τ_O , is determined by observing the decay of the main peak in the series of spectra which are taken to produce Figs. IV-d-f (see Fig. IV-h). The value of $\tau_{O \rightarrow i}^*$ which best fits the experimental data is primarily determined by the slope of the curve at $t = 0$, as can easily be seen by observing that the limiting form of IV-6 as $t \rightarrow 0$ is (to first order in t)

IV-h. Measured lifetime of 25f obtained from SFI
spectra.

$$N_i(t) \cong N_o(0) (1/\tau_{o \rightarrow i}^*) t \quad (IV-7)$$

Once these two parameters are fixed, τ_i is then varied to provide the best fit through the data at later times. The fitting algorithm is quite straightforward in that, if τ_o is assumed known, then $\tau_{o \rightarrow i}^* (\tau_i)$ is influenced primarily by the behavior of the data only at early (late) times. Hence a more complicated least-squares fitting procedure is not necessary.

D. Agreement of Transition Rates with Theory

For large t ($t \gtrsim 4 \tau_o$), when the parent state peak has decayed away to a height comparable to the BB state peaks, the basic assumptions of the model are no longer valid. For times close to $t = 0$, however, the model is clearly applicable, since the initial growth of each of the BB peaks is attributable solely to transitions from the parent nf peak. The transition rates ($1/\tau_{o \rightarrow i}^*$) obtained from the model fit are therefore expected to yield good values for the total transition rates from the parent nf state to the n'g and n"d states which comprise a single BB peak. These total transition rates are listed in Table IV-1 for a number of nf $\rightarrow$ n'g, n"d combinations.

Also shown in Table IV-1 are transition rates calculated theoretically using the quantum defect theory, which was discussed in Chapter II. The agreement between the total observed rates and the total calculated rates is generally satisfactory. The calculated rates in all cases fall within the estimated error bars of the measured rates.

Table IV-1. Measured and calculated transition rates for BB-induced photoexcitation. The calculated transition rates from the parent f states given in column 1 to the appropriate d and g states are shown in columns 3 and 5. The total calculated transition rates appropriate to a single BB peak are given in column 6 and are to be compared with the measured transition rates (obtained from the modeling procedure) shown in the last column. The larger lower error bars on the first BB peaks are due to uncertainties in subtracting the contribution from the parent peak.

n _f	n _g	$1/\tau_{f+g}^*$ (sec ⁻¹)	n ["] d	$1/\tau_{f+d}^*$ (sec ⁻¹)	$1/\tau_{total}^*$ (sec ⁻¹)	$1/\tau_{measured}^*$ (sec ⁻¹)
20	21	3224	23	4866	8090	7500 ± 1500 7500 ± 2300
	22	1602	24	994	2596	2400 ± 500
	23	980	25	464	1444	1300 ± 300
24	25	2110	27	3567	5677	7500 ± 1500 7500 ± 2300
	26	1075	28	749	1824	2000 ± 400
	27	674	29	359	1033	1100 ± 200
25	26	1919	28	3321	5240	7500 ± 1500 7500 ± 2300
	27	981	29	701	1622	1800 ± 400
	28	618	30	338	956	1100 ± 200

E. Lifetimes of the BB Peaks

It is interesting to note that the $f \rightarrow g$ transition rate is greater than the $f \rightarrow d$ rate for all the BB peaks presented in Table IV-1 except for the first ones (the BB peaks closest to the main peak). In these peaks, the $f \rightarrow d$ transition rate in fact dominates. The preponderance of the shorter-lived d state in the first BB peaks results in a shorter aggregate lifetime for these peaks as compared to the observed lifetimes for the subsequent peaks, as is evident from Table IV-2.

An exact interpretation of the model lifetimes obtained for the BB peaks is not possible, however, in the absence of more precise knowledge of the lifetimes of xenon d and g states. These lifetimes cannot be measured in situ in the manner that the f state lifetimes can, nor is there any information available in the literature on the lifetimes of highly excited xenon d and g states.

We have attempted to calculate these lifetimes by using the quantum defect method, as discussed in Chapter II. The results of the calculation are presented in Table IV-3. If these lifetimes are used in conjunction with the calculated transition rates in Table IV-1 to produce a two-state model fit through the data in Fig. IV-d, the solid curve in Fig. IV-i results. As can be seen from Fig. IV-i, the theoretical curve does not reproduce the data very convincingly. In general, the calculated lifetimes appear consistent with the

Table IV-2. Aggregate lifetimes of the BB peaks identified in Table IV-1 as obtained from the modeling procedure. The shorter lifetimes of the first peaks are probably due to a greater contribution from the d state, are reflected in the transition rates of Table IV-1. Peaks numbered 1 are composed of $(n+1)g$ and $(n+3)d$, etc.

parent nf state	BB peak no.	τ (μ sec)
20	1	8 ± 3
	2	15 ± 5
	3	17 ± 6
24	1	12 ± 4
	2	24 ± 8
	3	30 ± 10
25	1	12 ± 4
	2	24 ± 8
	3	29 ± 10

Table IV-3. Calculations of the lifetimes of the d and g states listed in Table IV-1 which are excited from Xe(25f), using the quantum defect method. Lifetimes include BB depopulation mechanisms. For reference, the hydrogenic lifetime (without BBR) of 26g is 30.7 μ sec.⁽⁵⁸⁾

d state	τ_d (μ sec)	g state	τ_g (μ sec)
28 d	6.4	26 g	17
29 d	7.1	27 g	19
30 d	7.8	28 g	21

IV-i. Theoretical model fit through the data of Fig. IV-d using calculated transition rates and lifetimes for Xe(26g) and Xe(28d).

observed BB peak lifetimes only to within a factor of two or three. Better agreement cannot be expected with this calculation, as the quantum defect wave function does not accurately represent the ground state and low-lying excited state wave functions of rare gas atoms.^(36,55)

F. Cooling the Environment of the Rydberg Atoms

When the box was cooled to liquid nitrogen temperature, the photoexcitation signal decreased dramatically, as shown in Figs. IV-j-m. The "hot" and "cold" spectra represented in each figure were taken under similar conditions of laser power and metastable beam density, so as to provide for nearly identical Rydberg production rates. Nonetheless, a small correction has been applied to the raw data to ensure that the pairs of BB spectra in Figs. j-m correspond to the same Rydberg production rate at $t = 0$.

Since the apparent lifetime of each state changes slightly as the temperature of the environment is changed, the ratios of the areas of the peaks are still not exactly equal to the ratios of the transition rates (see Eq. IV-6). The apparent lifetimes of several nf states have been measured at both room and liquid nitrogen temperatures. The difference in the lifetimes at the two temperatures is small ($\sim 10\%$) and agrees with quantum-defect predictions (see Table IV-5, this section).

In light of this agreement, the quantum defect theory is used to calculate the change in the total BB depopulation rates of the parent nf states and the appropriate d and g

IV-j. Effect of reduced temperature on the size of BB peaks populated by photoexcitation from Xe(23f). The BB SFI spectra were obtained at 300K (upper curve) and 90K (lower curve). Both spectra are normalized to the same Rydberg production rate at $t = 0$, and both spectra were taken at $t = \underline{5 \mu\text{sec}}$.

IV-k. Effect of reduced temperature on the size of BB peaks populated by photoexcitation from Xe(25f). The BB SFI spectra were obtained at 300K (upper curve) and 90K (lower curve). Both spectra are normalized to the same Rydberg production rate at $t = 0$, and both spectra were taken at $t = 8 \text{ } \mu\text{sec}$.

IV-1. Effect of reduced temperature on the size of BB peaks populated by photoexcitation from Xe(27f). The BB SFI spectra were obtained at 300K (upper curve) and 90K (lower curve). Both spectra are normalized to the same Rydberg production rate at $t = 0$, and both spectra were taken at $t = \underline{8 \mu\text{sec.}}$

IV-m. Effect of reduced temperature on the size of BB peaks populated by photoexcitation from Xe(29f). The BB SFI spectra were obtained at 300K (upper curve) and 90K (lower curve). Both spectra are normalized to the same Rydberg production rate at $t = 0$, and both spectra were taken at $t = \underline{9 \mu\text{sec}}$.

states at the two temperatures for each peak in Figs. IV-j-m. This information is in turn used to estimate the change in the total observed lifetimes of the parent nf peaks and the BB peaks (τ_o and τ_i in Eq. IV-6). The resulting correction to the measured ratios of the peak areas at the two temperatures amounts to only about a 10% effect in all cases.

The corrected ratios are presented in Table IV-4 under the column heading $\frac{300}{90} R_{\text{meas.}}$. Also shown in Table IV-4 are the results of a model calculation of the ratios of the appropriate transition rates at 300K and 90K. The uncertainty in the calculated ratios is primarily due to the fluctuation of the box temperature as data are being accumulated, although a small error is associated with uncertainty in the radiation leakage factor discussed in Chapter III. The agreement between the measured and calculated ratios is quite satisfying.

As was mentioned previously, the lifetime of a Rydberg state is affected by the BB photon density it experiences (see Eq. IV-1). If the apparent lifetime is measured at two different temperatures, the observed difference in the lifetimes may be expressed as

$$\frac{1}{\tau_Y} - \frac{1}{\tau_Y'} = \frac{1}{\tau_Y^{BB}} - \frac{1}{\tau_Y^{BB'}} . \quad (\text{IV-8})$$

Table IV-5 compares the observed difference in lifetimes of three nf states with calculated differences in BB depopulation rates. Once again, the agreement is gratifying.

Table IV-4. Ratios of transition rates from a parent n_f state to the first three BB peaks for 300K and 90K are calculated and compared with observed ratios for $n = 23, 25, 27$ and 29. Error bars on the calculated ratios are associated with fluctuations in the box temperature.

nf	BB peak no.	$^{300}_{90}\text{R}$	
		calc.	meas.
23	1	$3.0 \pm .1$	$2.9 \pm .3$
	2	$3.3 \pm .2$	$4.0 \pm .4$
	3	$3.6 \pm .2$	$4.0 \pm .4$
25	1	$2.9 \pm .1$	$3.0 \pm .3$
	2	$3.2 \pm .1$	$3.5 \pm .4$
	3	$3.4 \pm .2$	$3.3 \pm .3$
27	1	$2.9 \pm .1$	$2.7 \pm .3$
	2	$3.1 \pm .1$	$2.8 \pm .3$
	3	$3.3 \pm .2$	$3.5 \pm .4$
29	1	$2.9 \pm .1$	$2.8 \pm .3$
	2	$3.0 \pm .1$	$3.3 \pm .3$
	3	$3.2 \pm .1$	$3.0 \pm .3$

Table IV-5. Effect of temperature on apparent lifetimes of Rydberg states. The differences in the inverse of the observed lifetimes ($1/\tau_n$) of xenon nf states at 300K and 90K are compared with the differences in the total calculated BB depopulation rates ($1/\tau_n^{88}$) for the same states at the two temperatures. Also shown, in the last column, is the percentage change in the observed lifetimes in going from 300K to 90K.

nf	$(1/\tau_n^{BB})_{300} - (1/\tau_n^{DB})_{90}$ (sec ⁻¹)	$(1/\tau_n)_{300} - (1/\tau_n)_{90}$ (sec ⁻¹)	$\Delta\tau_{300+90}$ (%)
20	22000	17000 ± 8000	7
25	15000	15000 ± 7000	11
26	14000	15000 ± 7000	13

Also shown in Table IV-5 are the percentage changes in the total lifetimes in going from 300K to 90K. As was earlier asserted, the difference is small. This is in marked contrast to the case of sodium np states, where the calculated BB induced depopulation rate exceeds the calculated spontaneous decay rate.⁽⁴⁸⁾

G. Stimulated Emission

In addition to the photoexcitation signals which have been described, photo-d-excitation or stimulated emission has also been observed. Since, in this case, states with term energies lower than that of the parent nf state are being accessed, the field ramp must be increased beyond what is sufficient to ionize the parent nf state in order to observe this effect.

In Fig. IV-n a BB spectrum of 26f at $t = 5 \mu\text{sec}$ is shown in which the field ramp attains a sufficiently high value to ionize several BB-populated Rydberg states with term energies less than that of the parent state. To the left of the peak associated with the 26f state the now-familiar photoexcitation peaks appear. Due to experimental conditions, the peak-to-peak overlap in this spectrum is more severe than in Fig. IV-b. The peak identification given at the bottom of the figure may seem less convincing as a result of this smearing, but by tuning the laser to successively higher f states the position of the BB peaks on this ramp can easily be determined unequivocally. Nevertheless, the overlap between the parent f state and the first BB peak is so pronounced that the population of the first peak cannot be determined.

IV-n. BB-induced photoexcitation and photo-de-excitation (stimulated emission) of Xe (26f) atoms. The ionizing voltage ramp is such that the BB features are not well resolved. There is considerable overlap between the main peak and the two adjacent BB peaks. For easy reference to Table IV-6, the BB peaks are assigned positive and negative integer values according to whether they arise from photoexcitation or photo-de-excitation, respectively. The spectrum was taken at $t = 5 \mu\text{sec}$.

To the right of the large main peak, at higher field strengths, there appear two pronounced peaks which are associated with the product states of BB-induced stimulated emission and subsequent decay of the 26f state. These peaks are labeled with negative numbers, while those peaks to the left of the 26f peak are labeled with positive numbers. A third stimulated emission peak, labeled -1, is actually present, but is completely obscured by the primary peak.

The BB model has been used, along with the lifetime of the parent nf state and estimates of the lifetimes of the BB peaks, to deduce a total transition rate from the sizes of the BB peaks at $t = 5 \mu\text{sec}$. These measured feeding rates are compared in Table IV-6 with the total calculated transition rates for a number of peaks. The agreement for both the photoexcitation and photo-de-excitation peaks is gratifying. The calculated rates for the BB peaks arising from stimulated emission include a small ($\sim 20\%$) contribution due to spontaneous radiative decay of 26f to lower lying states.

Table IV-6. Measured and calculated photoexcitation
and photo-de-excitation rates from xenon
26f. The peak numbers correspond to those
at the bottom of Fig. IV-n.

Peak no.	$1/\tau^*$ calc. (sec ⁻¹)	$1/\tau^*$ meas. (sec ⁻¹)
-3	666	540 ± 130
-2	1065	1200 ± 1200
-1	2378	--
1	4864	--
2	1568	1740 ± 350
3	893	790 ± 160

APPENDIX A

MCA Dead Time Correction

Let C_k be the recorded number of events in the k^{th} MCA channel, C_k^* as the "true" number of events that the MCA would have registered had there been no other channels to stop it, p_k is the probability of an event occurring during the time that the k^{th} channel is active (p_k is assumed to be $\ll 1$), n_k the number of repetitions of the experiment experienced by the k^{th} MCA channel during L laser shots. Thus,

$$C_k = p_k n_k \quad (\text{A-1})$$

and
$$C_k^* = p_k L \quad (\text{A-2})$$

We need to solve (A-2) for C_k^* , the corrected number of events. The probability p_k must thus be solved empirically, using the following iterative procedure. Consider the first channel ($k = 1$), for which there is no dead time correction. In this case $n_1 = L$, so that

$$C_1 = p_1 L \quad (\text{A-3})$$

from Eq. (A-1). For the second MCA channel, there exists the possibility that an event registered in the first MCA channel will prevent the second channel from registering an event during certain laser shots. The number of repetitions of the experiment that channel 2 will be enabled will be less than L by the number of times an event was registered in channel 1.

Thus we have that

$$\begin{aligned} n_2 &= L - p_1 L \\ &= L - C_1 . \end{aligned} \quad (\text{A-4})$$

From Eq. (A-1), it is obvious that

$$C_2 = p_2 (L - C_1) . \quad (\text{A-5})$$

It is easy to see that, in general, the k^{th} channel will be disabled every time an event is registered in any j^{th} channel, where $j < k$:

$$n_k = L - \sum_{j=1}^{k-1} C_j \quad (\text{A-6})$$

so that

$$C_k = p_k \left(L - \sum_{j=1}^{k-1} C_j \right) \quad (\text{A-7})$$

Equation (A-7) trivially yields an expression for p_k :

$$p_k = C_k \left(L - \sum_{j=1}^{k-1} C_j \right)^{-1} \quad (\text{A-8})$$

Finally, substituting Eq. (A-8) into Eq. (A-2), we arrive at the expression

$$C_k^* = C_k \frac{L}{L - \sum_{j=1}^{k-1} C_j} \quad (\text{A-9})$$

Typically, C_k^* is larger than C_k by 10-30%.

APPENDIX B

When the box was cooled another, initially unexpected, effect was observed. If the voltage ramp was fixed (i.e., same slew rate and same $V_{\max}$ as at room temperature) the peaks in the BB SFI spectrum were shifted towards lower channel numbers (lower voltages). As the box was allowed to return to room temperature, the peaks returned to their original positions. Evidently, the shift was due to the contraction of the box as the temperature of the box was decreased. As a result, the separation between the two grids in the interaction region was reduced, producing a larger field strength in the interaction region for the same applied voltage.

The amount of contraction may be deduced by use of a field ionization technique originally due to West.⁽¹¹⁾ Rather than measure the differential ionization signal per time increment, dS/dt , one may also measure the total integrated ionization signal as a function of the maximum applied voltage, $V_{\max}$. Instead of using an MCA, one merely positions an electronic "gate" over the entire voltage ramp and counts, by use of a scaler, the total number of ionization events that occur at any point on the ramp. As $V_{\max}$ is increased, a sharp threshold in the ionization signal will be observed at that voltage, V_c , that corresponds to the critical field E_c , of the Rydberg state under study. The advantage of this technique is that detailed information about the ramp and delay times are not necessary to pinpoint the characteristic critical voltages of Rydberg states. A number of xenon nf states may then be studied in quick succession while the box is cold, and

their critical voltages compared with those measured at room temperature. In this manner, a consistent offset of $\sim 3\%$ was observed in the critical voltages of xenon nf states between box temperatures of 300K and 90K. This is a larger contraction effect than one would expect if just the contraction of the copper spacing ring separating the two grid structures (Fig. III-e) were taken into account, but is probably not unreasonable considering the complicated nature of the copper-teflon-steel sandwich arrangement.

The offset of the peaks in the "cold" BB SFI spectra may be accounted for by carefully mapping out the voltage ramps used for the temperature comparison. From a knowledge of dE/dt obtained from the field map, and dS/dt (the raw MCA data), one may obtain fairly straightforwardly dS/dE , or a "constant field" SFI spectrum. Using the same voltage ramp (dV/dt) but a different (3% smaller) grid separation, a different field ramp (dE/dt) is obtained for liquid nitrogen temperatures. If the constant field spectra are compared at the two temperatures, the peaks should line up, which they do fairly well.

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