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# COLLEGE ON ATOMIC AND MOLECULAR PHYSICS: PHOTON ASSISTED COLLISIONS IN ATOMS AND MOLECULES

(30 January - 24 February 1989)

## HIGHLY EXCITED ATOMS: CREATION & ANNIHILATION

Lecture 1

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# HIGHLY EXCITED ATOMS: CREATION AND ANNIHILATION

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## OUTLINE FOR LECTURE #1

1. Review of some important concepts.
2. Rydberg atoms and their properties - Rydberg series.
3. Why study Rydberg atoms?
4. Detection of Rydberg atoms - ease of ionization.
5. Effects of ambient temperature (blackbody radiation) on Rydberg atoms.
6. Some effects of collisions of Rydberg atoms with background atoms.

Where to obtain more information about Rydberg atoms:

Book -

*Rydberg states of atoms and molecules*
Edited by R. F. Stebbings & F. B. Dunning
Cambridge University Press (1983)

Review article -

*Rydberg atoms*
T. F. Gallagher
Reports of Progress in Physics **51**, 143 - 188 (1988)



## UNITS OF ENERGY

1 electron volt (eV) = the kinetic energy acquired by a particle with charge e in falling through a potential difference of 1 volt

$= 1.6 \times 10^{-19}$ joule

$= 1.6 \times 10^{-12}$ erg

Now the energy is related to the frequency $\upsilon$ (angular frequency $\omega$) by the Einstein relation

$$\text{Energy} = E = h\upsilon = \hbar\omega = hc/\lambda = \frac{12{,}400(\text{eV}\cdot\text{Å})}{\lambda}$$

where $\lambda$ is the wavelength of the radiation. We may write

$$\frac{1}{\lambda} = \frac{E(\text{in eV})}{12{,}400(\text{eV}\cdot\text{Å})}$$

If E = 1 eV, then

$$\lambda = 8.065 \times 10^{-5} \frac{1}{\text{Å}} \cdot \left(10^8 \frac{\text{Å}}{\text{cm}}\right)$$

$$= 8065 \text{ cm}^{-1}$$

The unit $\text{cm}^{-1}$ is regarded as a unit of energy. It is read "wave numbers".

Also

$$E = h\upsilon = (4.1354 \times 10^{-15} \text{ eV}\cdot\text{sec})\cdot\upsilon$$
$$= (4.1354 \times 10^{-15} \text{ eV}\cdot\text{Hz})\cdot\upsilon$$

Therefore, if E = 1 eV we have

$$\upsilon = \frac{1}{4.1354} \times 10^{15} \text{ Hz} = 2.42 \times 10^{14} \text{ Hz}$$

Thus, for transitions between low-lying excited states, ~eV, the frequencies are $\sim 10^{14}$ Hz, which correspond to wavelengths in the visible. This may be seen from the formula

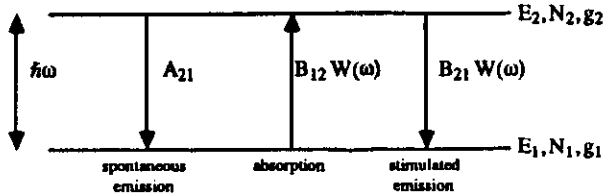
$$E(\text{in eV})\cdot\lambda(\text{in Å}) = 12{,}400$$

On the other hand, for transitions between levels separated by $\sim 10^{-3}$ eV, e. g. rotational levels of molecules, $\upsilon \approx 3 \times 10^{11}$ Hz.

# REVIEW OF SOME NECESSARY CONCEPTS

## Interactions of Atoms with Radiation

For a two level quantum mechanical system irradiated with an energy density given by W(ω) we have schematically




The three basic kinds of radiative processes.

where the A's and B's are the Einstein coefficients. The E's represents the energy of each level, $\hbar\omega$ their difference, the N's the population of each level and the g's the degeneracies of each level. Note that the Einstein coefficients are such that A and BW(ω) are *rates* , the units of which are $sec^{-1}$. Therefore, $A^{-1}$ is the lifetime τ of the upper level with respect to spontaneous emission.

For a multilevel system there will be an $A_{if}$ for each pair of levels so that the total rate of decay out of a particular state is the sum of the individual rates to each of the lower states. The lifetime is then given by

$$\tau_i = 1/\sum_f A_{if}$$

where the Σ is over all final states *f* of energy lower than the initial state *i*. Quantum mechanically $A_{if}$ is given by

$$A_{if} \propto (\hbar\omega)^3 \left| \int \psi_f^* \vec{p} \psi_i dv \right|^2$$

where the ψ's are the initial and final state wave functions and $\vec{p}$ is the electric dipole moment operator.





# REVIEW OF SOME NECESSARY CONCEPTS

## Heavy Body Collisions: Rate Constants and Cross Sections

For a heavy body collision of the type A + B → products, where A and B are atoms or molecules, the rate of collision at a particular velocity *v* is given by:

$$\text{Rate of collision} = \frac{dN_A}{dt} = -k(v)N_A N_B$$

where the N's are the densities of each species in atoms/$cm^3$ or $cm^{-3}$ and k(*v*) is the rate constant (not to be confused with Boltzmann's constant).

The collision cross section σ(*v*) at *v* is given by:

$$\sigma(v) = \int_0^\infty P(b)dA = \int_0^\infty P(b)[2\pi b db]$$

where b is the impact parameter and P(b) is the "opacity function", the probability of reaction as a function of impact parameter.

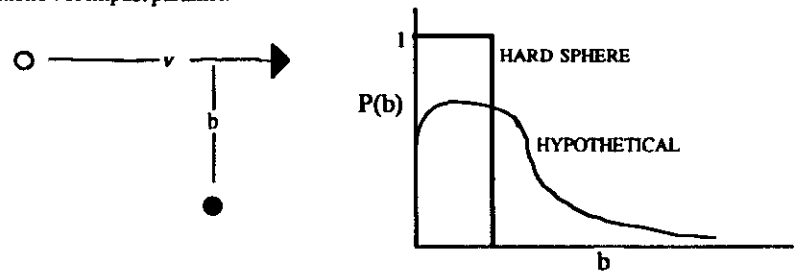



*Illustration of the impact parameter b and the opacity function.*

The rate of collision can also be given in terms of the cross section

$$\text{Rate of collision} = \frac{dN_A}{dt} = -\sigma(v) v N_A N_B$$

so that the rate constant and cross section are related by $k(v)=\sigma(v)v$. When an experiment is done however the atoms have a distribution of velocities f(*v*) which in many cases is simply the Maxwell-Boltzmann distribution. We must therefore integrate over this distribution in order to obtain the rate constant k that is measured, that is k, not k(*v*).

$$k = \int_0^\infty f(v)\,\sigma(v)\,v\,dv$$

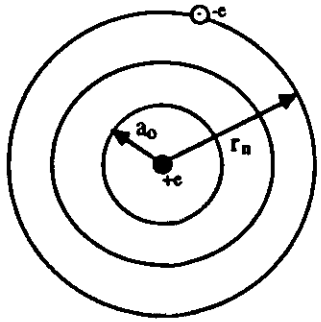
If σ(*v*) is only a slowly varying function of *v* then it may be removed from the integral. We have

$$k \approx \sigma(v) \int_0^\infty f(v)\,v\,dv \;\; \sigma(v)\bar{v}$$

where $\bar{v}$ is the average speed. For sodium at ~500 K, $\bar{v} \approx 10^5$ cm/sec.

## BOHR MODEL OF THE ATOM

Although the Bohr Model of the atom has its shortcomings, it is very useful to envision this model when performing many experiments in atomic physics. This is particularly true of experiments involving Rydberg atoms.




Bohr's Postulates:

1. The electron moves in a circular orbit about the nucleus under the influence of the Coulomb attraction between the electron and the proton.

2. The only possible orbits are those for which the angular momentum is an integral multiple of $\hbar$.

3. Despite the fact that the electron is continually accelerating, an electron moving in such an allowed orbit does not radiate energy. This is in contrast to the situation in classical electromagnetic theory.

4. Electromagnetic radiation *is* emitted if an electron initially moving in an orbit of energy $E_i$ discontinuously changes its motion so that it moves in a smaller orbit of total energy $E_f$. The frequency of the emitted radiation

$$\nu = \frac{(E_i - E_f)}{h} = \frac{\Delta E}{h}$$





## BOHR ATOM (continued)

Angular momentum = mvr = $n\hbar$ where m and v are the mass and velocity of the electron.

Also, the Coulomb force = centrifugal force:

$$\frac{1}{4\pi\varepsilon_o}\cdot\frac{e^2}{r^2} = \frac{mv^2}{r}$$

The total energy is

$$E = \frac{1}{2}mv^2 - \frac{1}{4\pi\varepsilon_o}\cdot\frac{e}{r} = -\frac{1}{4\pi\varepsilon_o}\cdot\frac{e^2}{2r}$$

Combining these three equations and using the dimensionless fine structure constant $\alpha$ defined as

$$\alpha = \frac{1}{4\pi\varepsilon_o}\cdot\frac{e^2}{\hbar c} \approx \frac{1}{137}$$

we have

$$v = \frac{\alpha}{n}c \quad \& \quad r_n = n^2 a_o$$

with

$$a_o = \frac{\hbar}{m\alpha c}$$

and

$$E_n = -\frac{1}{2}[mc^2]\cdot\frac{\alpha^2}{n^2} = -\frac{R_\infty}{n^2}$$

The last equation is known as the Rydberg equation and the constant $R_\infty$ is known as the Rydberg constant. It is given by

$$R_\infty = \left[\frac{1}{4\pi\varepsilon_o}\right]^2\cdot\frac{me^4}{4\pi\hbar^3 c}$$

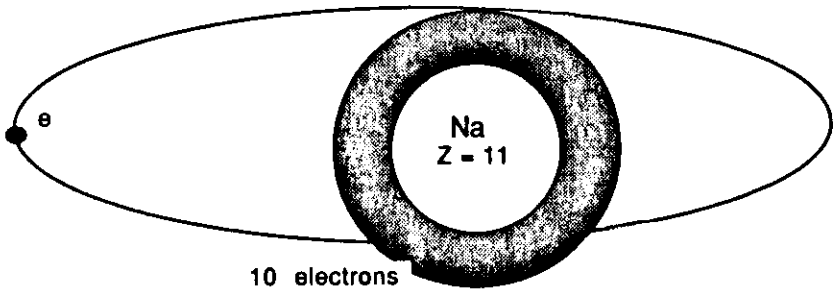
$$= 13.6 \text{ eV}$$

$$= 109{,}737.3 \text{ cm}^{-1}$$

## WHAT IS A RYDBERG ATOM?

Consider the sodium atom, electron configuration: $1s^2\ 2s^2\ 2p^6\ 3s^1$

Imagine the single 3s electron to be in a state of very high principal quantum number, n. Recall the Bohr atom.




The highly excited atom "sees" the 11 protons and the remaining 10 electrons at a distance. The electron therefore is under the influence of a net charge of +e so that if it does not penetrate the ion core it is under the influence of of very hydrogenlike potential, i. e. $V(r) = -e^2/r$.

Notice that for low angular momentum of this highly excited electron it will penetrate the core and thus be subject to the details of the structure of the core.

On the other hand, if the highly excited electron has high angular momentum then it will avoid the core and the energy levels are thus expected to be very hydrogenic.

**DEFINITION:** A Rydberg atom is one for which the energy levels are given by a Rydberg-like formula. For hydrogen -

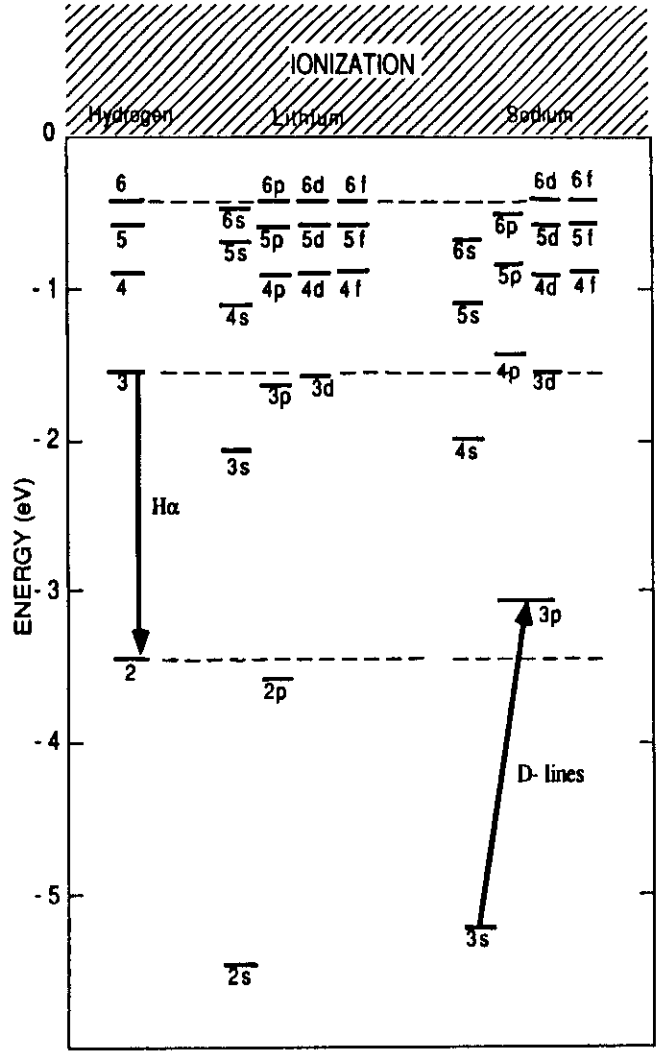
$$E_n = \frac{-R_\infty}{n^2}$$

where

n = principal quantum number








Some energy levels of hydrogen, lithium and sodium. Note that the high angular momentum states of Li and Na are hydrogenic while the low states are not.

The energy level formula may then be made to look like the familiar Rydberg formula for the energy levels of a hydrogen atom.

$$E_n = -\frac{R_\infty}{n^2}$$

For multielectron atoms, the Rydberg formula has the same appearance, but, in contrast to hydrogen, has an angular momentum dependence.

$$E_{n,\ell} = -\frac{R_\infty}{(n-\delta_\ell)^2}$$

where

$\ell$ = angular momentum quantum number

$\delta_\ell$ = quantum defect for a given angular momentum state. $\delta_\ell$ is essentially n-independent.

FOR SODIUM

$\delta_0 = 1.35$
$\delta_1 = 0.85$
$\delta_2 = 0.014$
$\delta_3 = 0.0015$

It is apparent that indeed, as the angular momentum increases and keeps the "Rydberg electron" away from the ionic core, the energy levels become hydrogenic.

The energy level structure is then similar to that of hydrogen in the sense that an infinite number of levels can be packed in below the ionization continuum. Unlike hydrogen however, each angular momentum state, $\ell$, has its own series of levels because $\delta$ is $\ell$-dependent.





## SOME PROPERTIES OF HIGHLY EXCITED ATOMS

| Quantity | Asymptotic n behavior | n = 1 | n = 30 |
|---|---|---|---|
| orbital radius | $n^2$ | 0.53 Å | 477 Å |
| cross sectional | $n^4$ | 0.9 Å$^2$ | $7 \times 10^5$ Å$^2$ area |
| orbital velocity | $n^{-1}$ | $2.2 \times 10^8$ cm/s | $7.3 \times 10^6$ cm/s |
| ionization potential | $n^{-2}$ | 5.1 eV (Na) | 0.015 eV |
| energy level separation | $n^{-3}$ | 2.1 eV (Na) | 0.001 eV |
| radiative lifetime (for a specific $\ell$-state) | $n^3$ | 16 nsec | $3 \times 10^4$ nsec |
| radiative lifetime ($\ell$-averaged) | $n^{4.5}$ | 16 nsec | 300 μsec |

All but the last two of these can be deduced from the Bohr model of the atom. The last two require knowledge of the wavefunctions for hydrogen atoms, which of course are not included in the Bohr model.

See

*Quantum Mechanics of One- and Two- Electron Atoms*
H. A. Bethe and E. Salpeter
(1977, Plenum Press)

## WHY STUDY RYDBERG ATOMS?

1. To a first approximation Rydberg atoms behave as hydrogen atoms with high principal quantum number, n. Therefore, deviations from hydrogenic behavior provide information about properties of the ionic core and its interaction with the valence electron.

2. All physical quantities vary rapidly with n. Thus, the scale and relative importance of the physical properties are quite different from those of moderately excited atoms.

3. Unusual properties: Electronic transitions in the microwave, huge dipole moments, etc.

4. Examination of the properties of Rydberg atoms may be made over a series of states. This permits systematic studies of the evolution of these properties as the bound electron approaches the continuum.

5. Studying series of states allows us to obtain insight into the quality of approximation methods used to compute the various atomic properties.

6. Rydberg atoms are much more sensitive to outside influence than are atoms in lower-lying states.

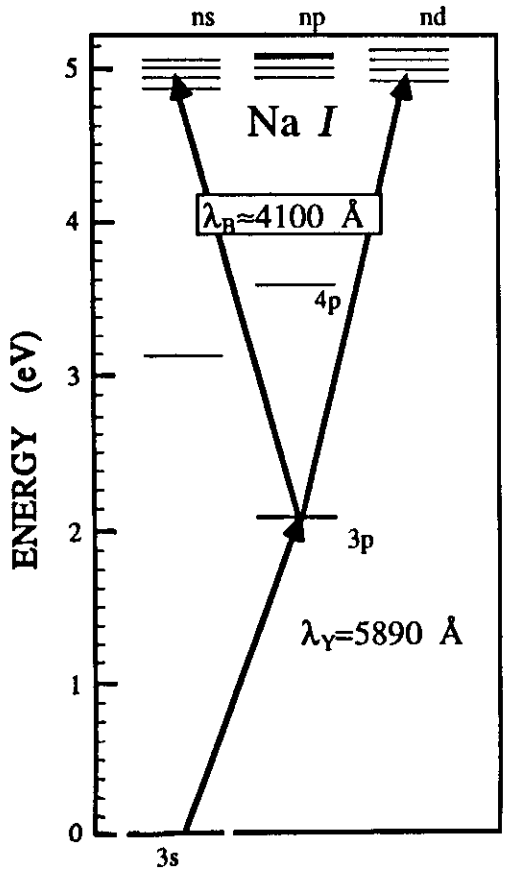
Example - It would require an electric field of enormous magnitude to ionize an atom in a low-lying state, but a field of $\geq$6 kV/cm can ionize a Rydberg atom having n=15. Thus, we may study atoms and their interactions using the extreme sensitivity of Rydberg atoms to make the effects observable.

Another example - The ionization potential of a ground state sodium atom is 5.1 eV while the average kinetic energy at 300 K is $\approx$1/40 eV = 0.025 eV. Therefore, collisions with other atoms in the mixture cannot result in ionization. At n = 33 however the ionization potential $\approx 13.6/33^2$ eV $\approx$ 0.0125 eV, so these atoms can easily be ionized in thermal collisions.





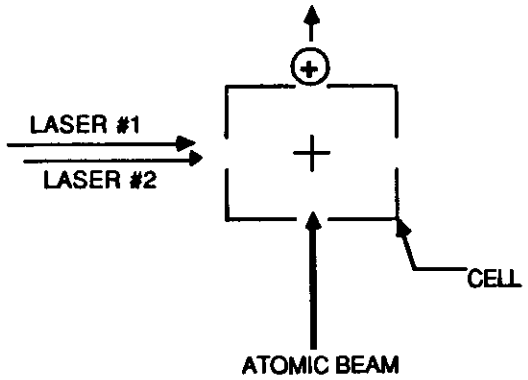
## CREATION OF SODIUM RYDBERG ATOMS BY 2-STEP LASER EXCITATION



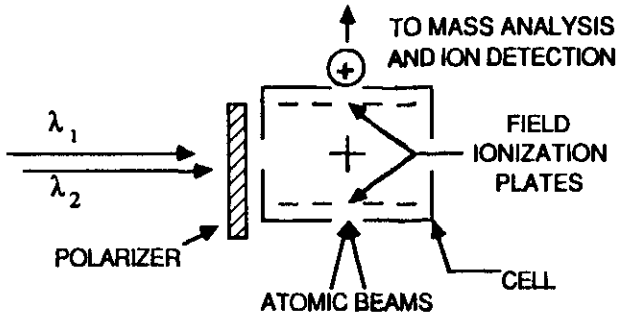

By using two laser beams we may sequentially excite alkali atoms to very high-lying Rydberg states. Alkali atoms are desirable because they have low ionization potentials and contemporary tunable lasers are most efficient in the visible region of the spectrum. Recall that

$$E(\text{in eV})\lambda(\text{in Å}) = 12{,}400$$

## SCHEMATIC DIAGRAM OF A TYPICAL APPARATUS FOR PRODUCING RYDBERG ATOMS



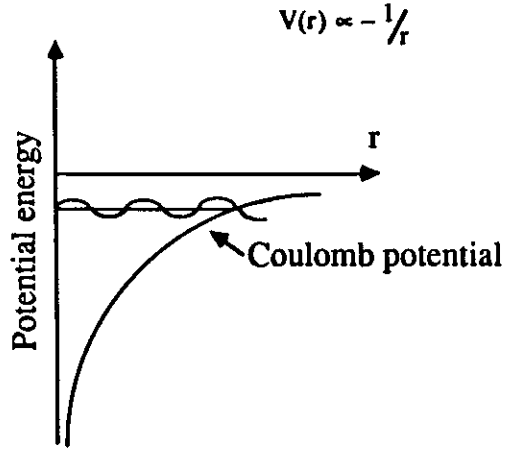

**MORE DETAIL**

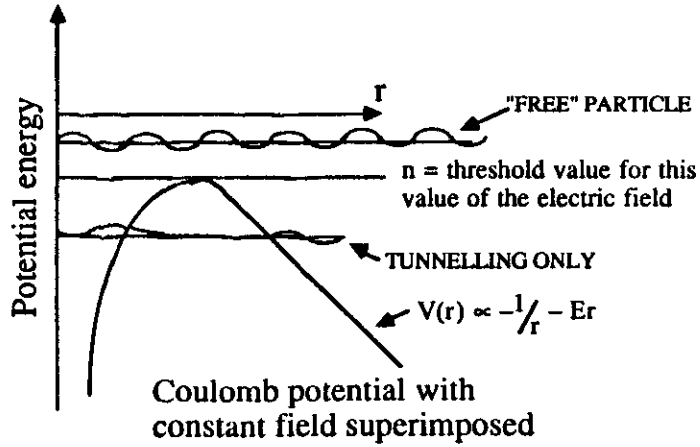




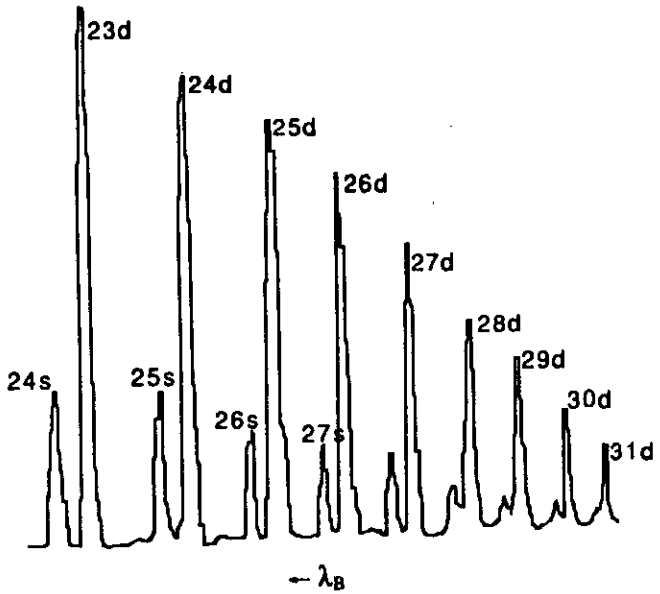



# DETECTION OF RYDBERG ATOMS BY FIELD IONIZATION



## PROMPT (30nsec) FIELD IONIZATION OF SODIUM




The peak heights are indicative of the initial population of the particular state because the field ionization is *prompt*. This means that no other ionization mechanisms have time to compete with field ionization. We see that the peak heights fall off roughly as $n^{-3}$, which is appropriate for a transition to a specific angular momentum state, in this case either 3p→nd or 3p→ns.





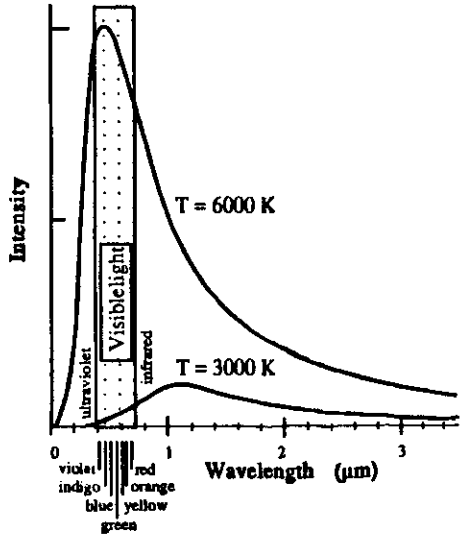
## EFFECTS OF BLACKBODY RADIATION ON RYDBERG ATOMS

Because the energy levels are so closely spaced for high values of n, in contrast to the situation for low-lying levels, blackbody can have a significant effect on Rydberg atom.

Recall that all bodies at finite temperature radiate. An ideal radiator, a blackbody, radiates in accordance with the Planck law.

$$p(\upsilon)d\upsilon = \frac{8\pi h\upsilon^3}{c^3}\frac{1}{[\exp(h\upsilon/kT)-1]}$$

where $p(\upsilon)$ is the energy density, loosely speaking the "intensity", and $k$ is the Boltzmann constant.



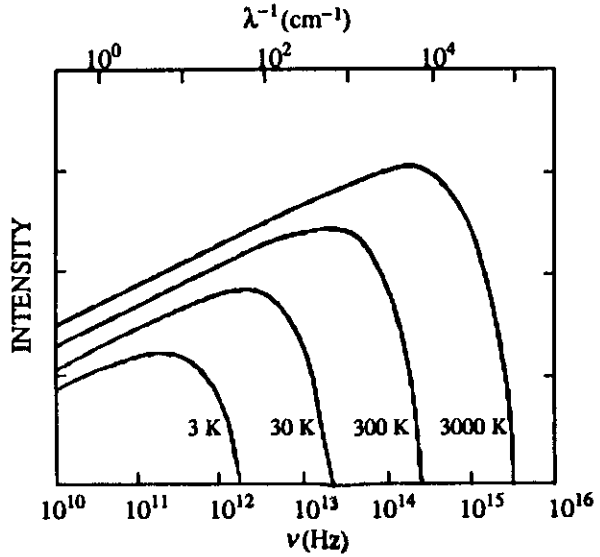

*Spectrum of frequencies emitted by a blackbody at two different temperatures. The 6000 K spectrum is approximately that emitted by our sun. On this scale a room temperature, 300 K, blackbody spectrum would almost coincide with the horizontal axis.*

Note that the Wein displacement is described by:

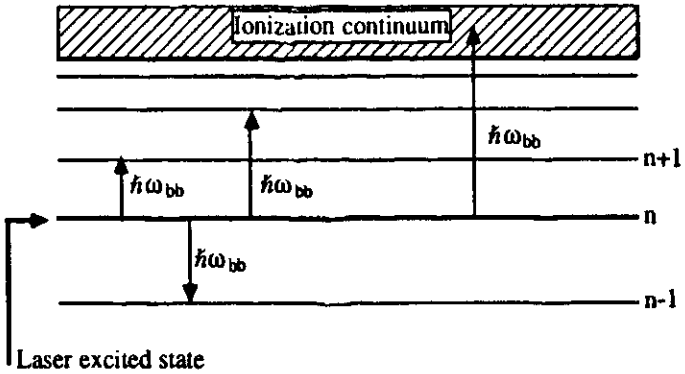
$$\lambda_{max}\cdot T = 28.9 \times 10^6\ \text{Å}\cdot\text{K}$$

so that a 6000 K blackbody, roughly comparable to our sun, radiates maximum intensity at ~5000 Å, i. e. in the visible region of the spectrum. A 300 K blackbody radiates maximum intensity at ~$10^5$ Å corresponding to a photon of energy ~0.1 eV. This means that there will be appreciable radiation in the tail of such a distribution that can affect highly excited Rydberg atoms.

**ANOTHER PLOT OF BB RADIATION**




BECAUSE THE RYDBERG ATOMS ARE SO FRAGILE THEY MAY BE DESTROYED (IONIZED) BY THERMAL COLLISIONS OR EVEN IONIZED BY BLACKBODY RADIATION. IN FACT, AN ATOM IN A GIVEN EXCITED STATE MAY UNDERGO AN INDUCED TRANSITION TO A LOWER OR HIGHER STATE BY PHOTONS IN THE BLACKBODY SPECTRUM.



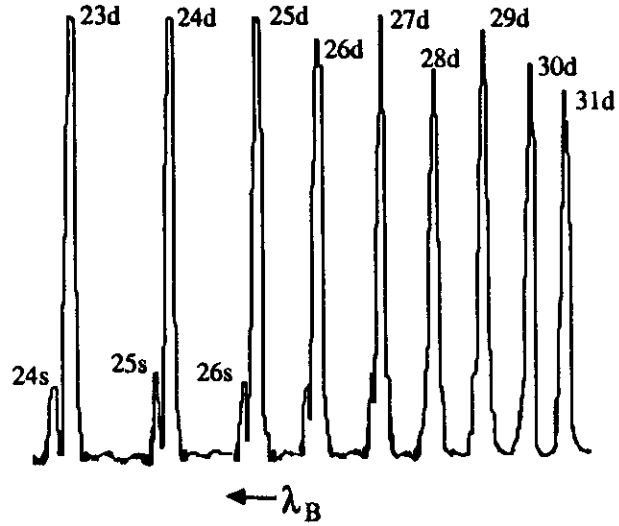

Two possible effects of blackbody radiation:

1. Photoionization (destruction of Rydberg atoms).
2. State-changing (destruction of the state-selectivity provided by laser excitation).





Consider photoionization by blackbody radiation (BBPI).
The spectrum below was acquired with no field ionization plates in the cell. The ion signal was that measured in between pulses from the 10 Hz pulsed lasers. Therefore, the signal that is observed is that due to *any* combination of events that lead to ionization, excluding field ionization. Possible ionization mechanisms include BBPI and collisional ionization, collisional ionization referring to collisions between Rydberg atoms and ground state atoms or even Rydberg-Rydberg collisions. It is however known that the probability of collisional ionization at the relatively low atomic beam density used in this particular experiment makes this ionization mechanism negligible here.




Note that, in contrast to the case for prompt field ionization, the peak heights in this spectrum are essentially the same for each set of states.

This observation leads to an important conclusion about angular momentum changing in $Na^{**}$-Na collisions. The cross section for these "$\ell$-mixing" collisions is enormous.

We reach this conclusion by examining the reason for the independence of the peak heights on n in the region shown above.

It can be shown that, if we assume that the time dependence of the population of Rydberg atoms $N^{**}(t)$ is given by a single exponential with lifetime $\tau_n$, i. e.

$$N^{**}(t) = N_{on}^{**}\exp[-\frac{t}{\tau_n}]$$

where $N_{on}^{**}$ is the initial concentration of Rydberg atoms, then the total number of ions from blackbody radiation of a particular state characterized by principal quantum number n is given by

$$Q_n = KR_nN_{on}^{**}\tau_n$$

See C. E. Burkhardt *at al*, Phys. Rev. A 34, 80 (1986).

Now, as indicated in the last equation, each of the last three quantities depend on n.

$N_{on}^{**}$ is proportional to $n^{-3}$ because it is produced by transitions to a specific value of $\ell$, that is s or d.

$R_n$ can be be shown to be given in this region by

$$R_n = \text{Constant} \times \frac{(E_n)^2}{\left\{\exp[\frac{E_n}{kT}] - 1\right\}}$$

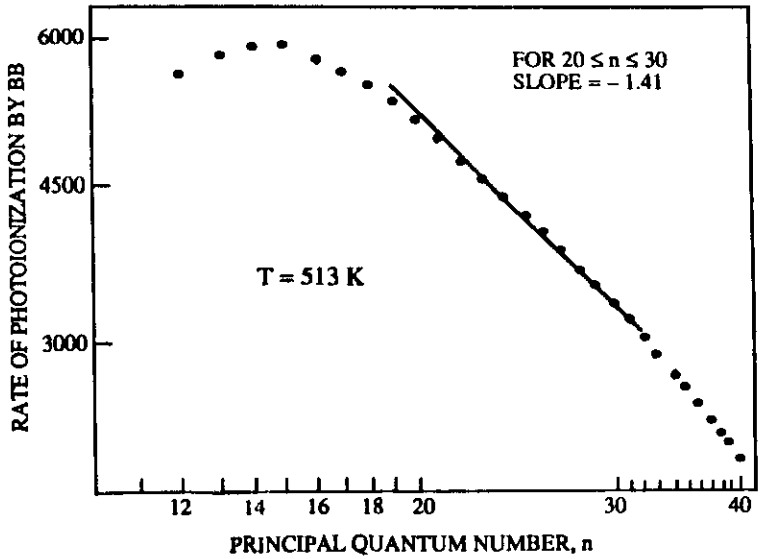
where $E_n$ is the ionization potential of the Rydberg atom.

See W. P. Spencer et al *Photoionization by blackbody radiation*, Phys. Rev. 26, 1490 (1982).





Below is a graph of this function for the principal quantum numbers of interest, $18 \leq n \leq 30$.




The ordinate scale was determined by measurement of the BBPI rate at n=18. In the region of interest n varies as $n^{-1.4}$.

We arrive at the following n-dependence for $Q_n$

$$Q_n \propto n^{-1.4}\cdot n^{-3}\cdot n^{x}$$

In order to satisfy the experimentally observed independence of $Q_n$ on n we must have $x \approx 4.4$.

But, the $n^x$ term represents the lifetime of the Rydberg state. This lifetime is proportional to $n^3$ if the Rydberg atoms remain in a single angular momentum state, the initially excited $\ell$. But the data indicate that $x \approx 4.4$ which is very close to the 4.5 that is characteristic of a mixed population on angular momentum states. We arrive at the important conclusion that the angular momentum of the Rydberg atoms is rapidly converted from a specific $\ell$-state to a nearly statistical distribution of $\ell$-states. This must occur in collisions and the $\ell$-mixing rate must be very high. The cross section for this process is $\sim 10^5$ Å$^2$, roughly the geometric size of the Rydberg atom.

**Conclusion: The state selectivity afforded by laser excitation is rapidly destroyed by collisions with background atoms.**

We have seen that even though a particular n$\ell$ state has been produced we have redistributed the population over all $\ell$ states by collisions. This can only be avoided if the density is kept low enough to preclude such collisions. If however the intent is to study collisional processes such as ionization in Rydberg-ground state atom collisions then the experiments will be performed with a distribution of $\ell$-states unless the cross section is appreciably larger than that for $\ell$-mixing. It is not!

We have also lost Rydberg atoms to photoionization by blackbody radiation.

In addition, the blackbody radiation can further destroy the state selectivity provided by laser excitation by redistribution of the states to neighboring n-levels.