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

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HIGHLY EXCITED ATOMS: CREATION & ANNIHILATION

Lecture 3

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HIGHLY EXCITED ATOMS: CREATION & ANNIHILATION

Lecture #3

OUTLINE FOR LECTURE #3

1. Rydberg states vs. highly excited states
2. Perturbation of a Rydberg series
3. Consequences of perturbation of a Rydberg series
4. Collisions involving atoms having Rydberg and non-Rydberg states

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RYDBERG STATES AND NON-RYDBERG STATES

So far we have discussed interactions of highly excited sodium atoms with other atoms and with radiation. Sodium has very regular Rydberg series, that is, the energies are given by

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

and δ_ℓ is very nearly constant for each ℓ.

Because Na has a single electron (the 3s electron) outside a Ne-like core, promotion of this 3s electron results in these regular Rydberg series.

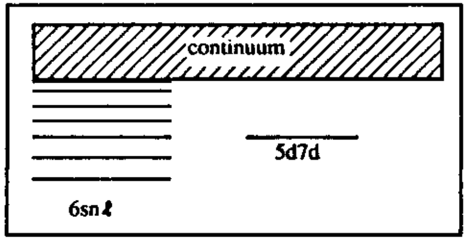
To excite a second electron in Na requires a great deal of energy, ~30 eV, because we must promote a 2p electron from the closed 2p shell. This is related to the fact that the first excited states of the rare gas atoms are very high-lying, ~16 eV for Ne. This is because an excited Ne is chemically similar to Na which has an ionization potential of 5.14 eV. Therefore, the first excited state of Ne must be ~5 eV from the Ne^+. Since ground state Ne has an ionization potential of 21 eV the first excited state must lie ~16 eV above the ground state. The result is that doubly excited states of Na have energy well above the first ionization potential of Na and rapidly autoionize in an Auger-like process

$$Na^{***} \rightarrow Na^+ + e + \text{kinetic energy}$$

where the *** signifies excitation above the 5.14 eV ionization energy of Na.

For a 2-electron atom such as Ba with its $(1s)^2 \ldots (4d)^{10}(6s)^2$ configuration $\{[Xe](6s)^2\}$, the two 6s electrons may be simultaneously excited and the energy of the resulting state less than the 5.21 eV ionization energy of Ba.

It is possible therefore to have two types of independent electron configurations with nearly the same energy



We may also say that δ_ℓ changes near the "interloper" doubly excited state which is also referred to as a valence state.

This independent electron picture ignores the interaction between the electrons. The presence of the interloper state will cause the true energy levels to deviate from the predictions of a Rydberg-like formula. We say that the Rydberg series is perturbed by the interloper state which, for this reason, is often referred to as a perturber state.

When we "turn on" the e-e interaction and treat it as a perturbation of the independent electron states we if course get new eigenstates and energy eigenvalues. Since the unperturbed states form a complete set however we may expand the new eigenfunctions on this complete set of unperturbed states.

In what follows we will solve this problem exactly under the assumption that only two of the independent electron states interact, the perturber state and one of the Rydberg states. This will simplify the problem and let us see the physics.

PERTURBATION OF A RYDBERG SERIES: BARIUM

Consider two nearly degenerate non-interacting levels for which we now turn on the e-e interaction. For barium, the atom of interest here, the independent electron configurations are $6sn\ell$ and 5d7d. We denote their wavefunctions by ϕ_R (for Rydberg) and ϕ_P (for perturber) respectively. They are eigenfunctions of the independent electron hamiltonian operator, H_o so that

$$H_o\phi_R = E_R\phi_R \quad \text{and} \quad H_o\phi_P = E_P\phi_P$$

Now consider the interaction, V, caused by the interaction between the electrons. The true hamiltonian is

$$H = H_o + V$$

The true wavefunctions Ψ_1 and Ψ_2 of the levels may be written as linear combinations of the ϕ's. If we assume that there are no adjacent levels so that only the two ϕ's above are included in the linear combination we have

$$\Psi = \alpha\phi_R + \beta\phi_P \quad \text{where} \quad H\Psi = E\Psi$$

We expect two new E's and two new Ψ's. We have

$$[H_o + V]\cdot[\alpha\phi_R + \beta\phi_P] = E[\alpha\phi_R + \beta\phi_P]$$

which, using the above conditions becomes

$$\alpha E_R\phi_R + \beta E_R\phi_P + \alpha V\phi_R + \beta V\phi_P = \alpha E\phi_R + \beta E\phi_P$$

Note that V is an operator, the E's are real numbers and the α's and β's may be complex.

Take the inner product of this equation, first with ϕ_R and then with ϕ_P. We get two equations:

$$[E - E_R]\alpha = V_{RR}\alpha + V_{RP}\beta \quad \& \quad [E - E_P]\beta = V_{PR}\alpha + V_{PP}\beta$$

$$\text{where} \quad V_{RP} = V_{PR} = \int_{\text{all space}} \phi_R^* V \phi_P \, d\tau = \int_{\text{all space}} \phi_P^* V \phi_R \, d\tau$$

This may be written more compactly in Dirac notation

$$V_{RP} = V_{PR} = <\phi_R|V|\phi_P> = <\phi_P|V|\phi_R>$$

We wish to solve for E, α and β subject to the normalization condition

$$|\alpha|^2 + |\beta|^2 = 1$$

The pair of equations has a nontrivial solution only if the determinant of the coefficients vanishes:

$$\begin{vmatrix} E - E_R - V_{RR} & -V_{RP} \\ -V_{PR} & E - E_P - V_{PP} \end{vmatrix} = 0$$

from which we get

$$E_\pm = \frac{E_R + E_P + V_{RR} + V_{PP}}{2} \pm \sqrt{\frac{[E_R + E_P + V_{RR} + V_{PP}]^2}{4} - (E_R + V_{RR})\cdot(E_P + V_{PP}) + |V_{RP}|^2}$$

Note that there are two energies corresponding to the + and − sign of the discriminant. The last equation is exact and shows that the "new" levels are more widely spaced than the unperturbed levels. They "repel" because of the ±.

If we turn off the interaction, that is $V \cong 0$, we get $E_+ = E_R$ and $E_- = E_P$ as we should. E_+ "fits'" into the Rydberg series because it is unaffected by the presence of the doubly excited state. But, as long as $V \neq 0$ then neither E_+ nor E_- fit into the Rydberg series. This is equivalent to saying that δ_ℓ changes as we go through the region of the interloper state.

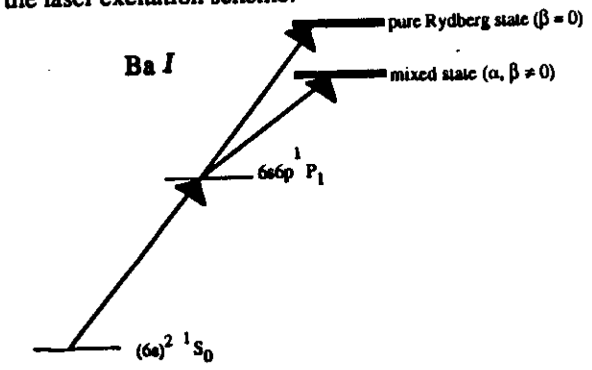
For each solution for the energy, E_+ and E_-, there will be a different set of α and β, i. e. α_+ and β_+ and α_- and β_-.

The true wavefunctions are

$$\Psi_+ = \alpha_+\phi + \beta_+\phi \text{ and } \Psi_- = \alpha_-\phi + \beta_-\phi$$

with eigenfunctions E_+ and E_-.

Now consider the laser excitation scheme:



The transition matrix element from the intermediate 6s6p $^1P_1$ state to the high-lying level is of the form

$$<\Psi_{\text{intermediate}}|p|[\alpha|\phi_R> + \beta|\phi_R>]$$

where **p** is the electric dipole operator.

$$\text{But,} \qquad <\Psi_{\text{intermediate}}|p|\phi_R> = 0$$

so that, if all other things are equal, the perturbed state population is reduced by $|\alpha|^2$ from that of the transition to a pure Rydberg state (for which $\alpha \cong 1$ and $\beta \cong 0$).

FRACTION OF 5d7d (DOUBLY EXCITED) STATE FOR SEVERAL STATES OF BARIUM

STATE DESIGNATION*	PERTURBER FRACTION (%) $[\|\gamma\|^2]$
13d $^3D_1$	0.05
5d7d $^3S_1$	0.90
-----	-----
14d $^1D_2$	0.25
14d $^3D_2$	0.10
5d7d $^3F_2$	0.40
----	----
16d $^1D_2$	0.00
5d7d $^3P_0$	0.58
18s $^1S_0$	0.35
----	----
18d $^3D_1$	0.20
5d7d $^1P_1$	0.75
----	----
26d $^1D_2$	0.125
26d $^3D_2$	0.13
5d7d $^1D_2$	0.365
27d $^1D_2$	0.189
27d $^3D_2$	0.009

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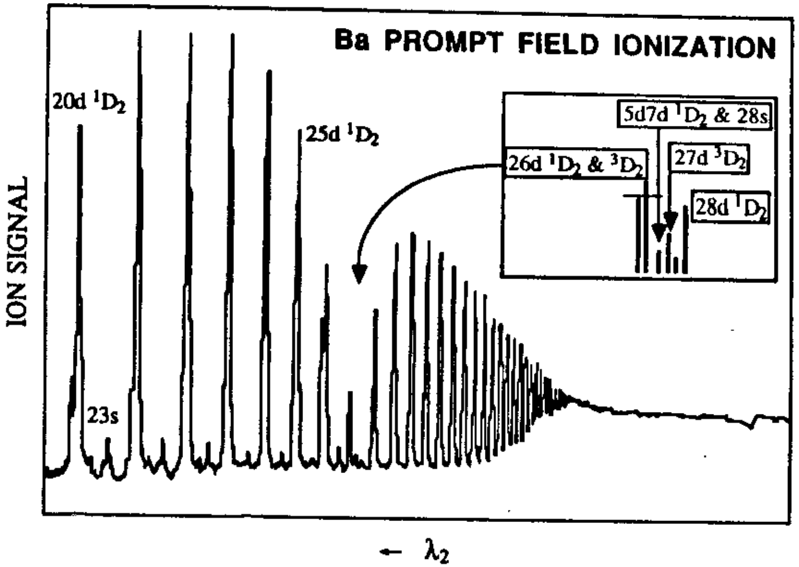
* These LS-coupling designations are merely names for the eigenstates of the true hamiltonian operator. For example, the state designated 5d7d $^1D_2$ (near 27d) has only 36.5% perturber character. The state designated 27d $^1D_2$ (seemingly a pure Rydberg designation) has 18.9% perturbercharacter.

The effects of the 5d7d states can be seen in a prompt FI spectrum of Ba.



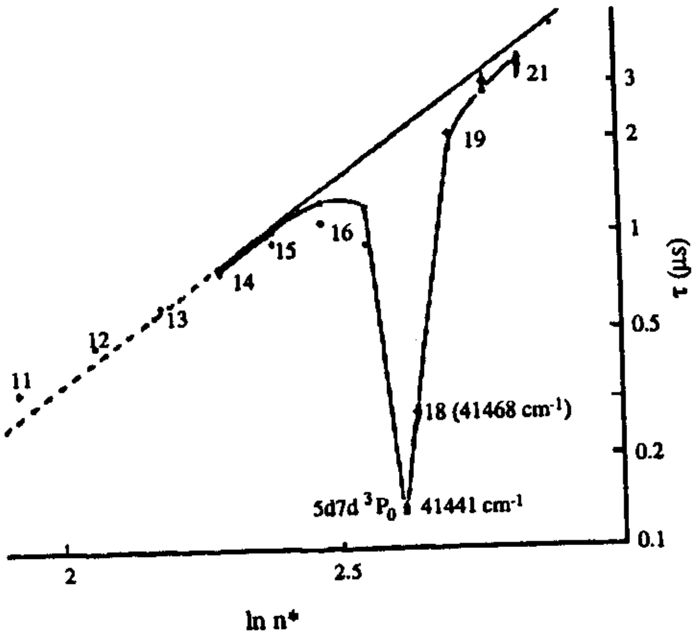
Note that the highly perturbed 5d7d $^1D_2$ and 27d $^1D_2$ states are not produced as efficiently by the laser excitation are the nearly pure Rydberg states.

Perturbed states also have shorter lifetimes than pure Rydberg states. This is because there is reasonably good overlap between the compact perturber portion of the wavefunction and the wavefunctions of lower-lying states. The shorter lifetimes of the perturber states permit them to radiatively decay before the "prompt" application of the field ionization, which is actually delayed ~200 nsec for the spectrum shown above. Nevertheless, the low yield is due, for the most part, to a zero contribution to the matrix element connecting the 6p $^1P_1$ state to the perturbed states by the perturber component of the true wavefunction, i. e.

$$<\phi_{6p}|p|\ \alpha\phi_R+\beta\phi_P> \approx <\phi_{6p}|p|\ \alpha\phi_R> \quad \text{because} \quad <\phi_{6p}|p|\ \phi_P> \approx 0.$$

LIFETIMES OF PERTURBED STATES

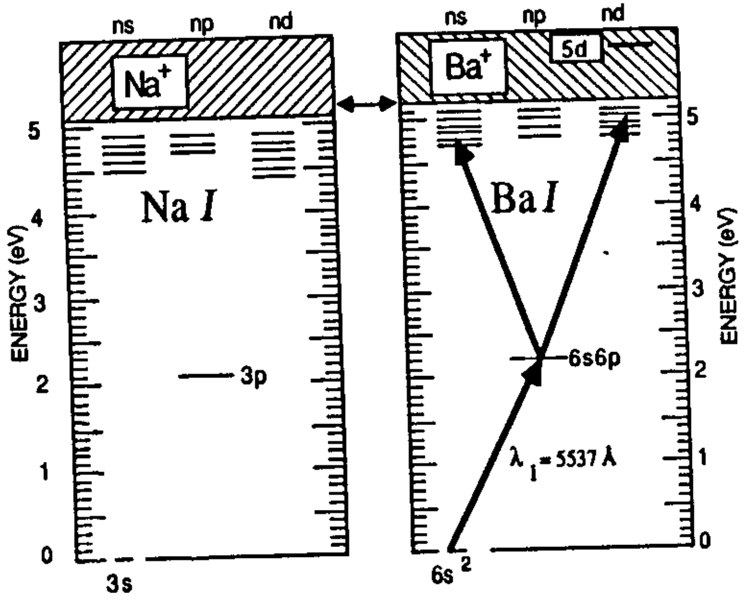
Effects of the 5d7d $^3P_0$ perturber on the lifetimes of the neighboring states that are designated by the LS-coupling notation, ns $^1S_0$. Taken from M. Aymar et. al. [J. Phys. B. 15,877 (1982)].



Ln-ln plot of experimental and theoretical lifetime values for J=0 states against the effective quantum number $n^* = n - \delta$. The straight line corresponds to $\tau = (n^*)^3/\gamma$ with $\gamma = 1190$. +: experimental values; dots: theoretical values.

COLLISIONS BETWEEN Ba** and Na(3s)

We may use the fact that barium has otherwise regular Rydberg series that are interrupted by the highly perturbed states as indicated in the lifetime plot shown above to contrast the reactive properties of Rydberg states with non-Rydberg states, in this case mixed Rydberg-valence states.



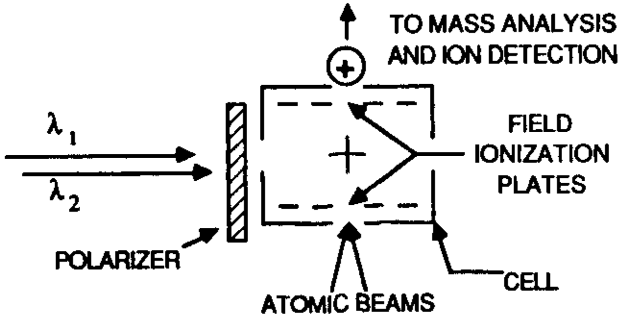
PENNING IONIZATION

Because the ionization potential of Na (5.14 eV) is lower than that of Ba (5.21 eV) it is possible to store enough energy in a Ba atom to ionize a ground state Na atom. This type of process is called Penning ionization. For Ba**-Na collisions there is a "threshold energy state" for this reaction to be energetically possible without conversion of kinetic energy of the Ba and Na atoms to internal energy to drive the reaction. For this case the threshold state is near n≈16d of Ba.

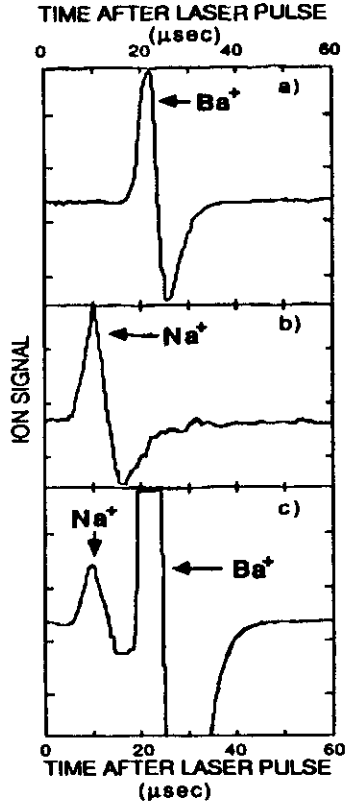
In equation form - $Ba^{**} + Na(3s) \rightarrow Na^+ + Ba + e$

EXPERIMENTAL CONSIDERATIONS

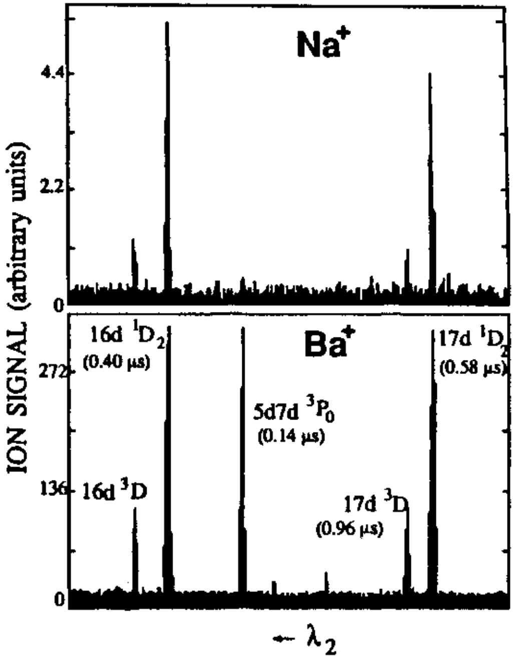
For these experiments we must be able to distinguish between Ba^+ (formed by any process) and Na^+. We thus add the capability of mass analysis.



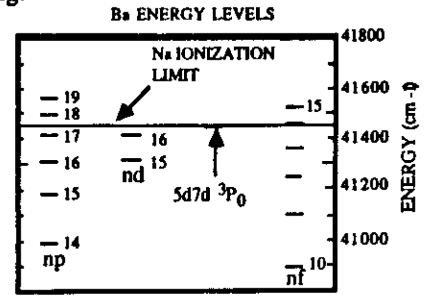
TIME OF FLIGHT SEPARATION OF Ba^+ AND Na^+



TYPICAL DATA



The lower spectrum is a field ionization spectrum of Ba^{**}. It serves to locate the wavelengths at which the Ba excitations occur and to indicate the relative populations of the laser-excited states. It was acquired with the time-of-flight (TOF) setting for Ba^+. The upper spectrum, acquired with the TOF setting for Na^+, shows that the highly perturbed 5d7d $^3P_0$ state is completely ineffective as a reactant for Penning ionization. A closer look at the energy level diagram shows that this is very surprising.



Notice that the perturbed level is within ~7 cm^{-1} of the ionization energy of Na.

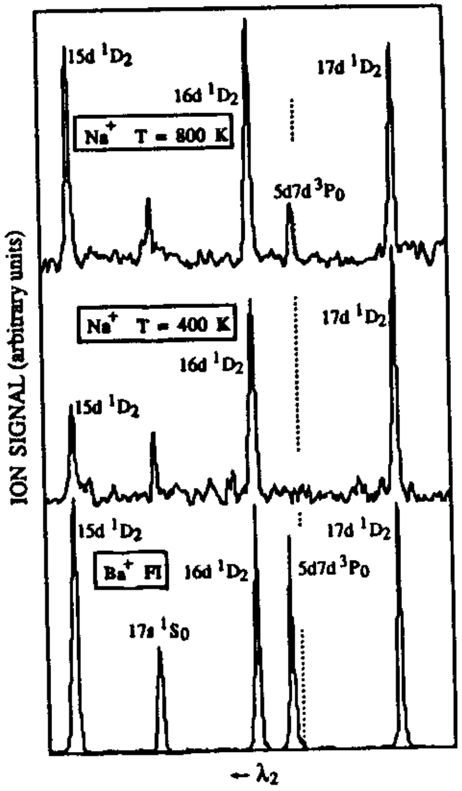
Recall that the average kinetic energy at 300 - 400 K is ~300 cm^{-1} so that there is sufficient kinetic energy to supply the meager 7 cm^{-1} that is required. The absence of Na^+ at the perturbed state is even more surprising when one considers that the pure Rydberg 16d $^1D_2$ state, for which Penning ionization is ~30 cm^{-1} deficient (endothermic), seems to be quite effective as a reactant, suggesting that, indeed, kinetic energy transfer is driving the reaction. In fact, we even see product Na^+ at the wavelength of the 15d $^1D_2$ state for which the reaction is ~150 cm^{-1} endothermic. It is true that the lifetime of the perturbed state is shorter than those of the pure Rydberg states, but only by a factor of ~3 at these relatively low quantum numbers.

Spectra taken at longer wavelengths do not show any product Na^+ at 14d and below. The onset of Penning ionization is therefore rather sharp as the threshold state is approached from below. The cross section is also observed to rapidly decrease as the energy exceeds threshold (becomes exothermic).

These experiments were however *not* performed in the cryogenic apparatus. What are the effects of blackbody radiation? Can blackbody radiation transfer the reactant from a low (unreactive) state to a higher (reactive) one? While we have not yet performed any collision experiments in the cryogenic apparatus, we can crudely examine the effects of blackbody radiation on the Penning process because of the threshold internal energy required to cause the reaction.

How do we do this? Since we can't cool the cell, we examine the effects of heating the cell.

The spectra shown below are analogous to those shown previously, but in this case we warmed the cell that defines the collision region. The temperatures indicated, 400 K and 800 K, are the thermocouple readings, not necessarily the actual blackbody temperatures. Nevertheless we will use them as an approximation to the blackbody temperatures.



Two differences in the Na^+ spectra are apparent.

1. The ratio of the Na^+ peak heights at the wavelengths of the Ba 15d and 16d states has increased [15d/16d] in the 800 K spectrum.
2. As before, there is no Na^+ signal at the location of the 5d7d $^3P_0$ state in the 400 K spectrum, but there is a small signal in the 800 K spectrum.

The cause of the first effect is equivocal. We might argue that blackbody radiation can excite the Ba(15d and 16d) to higher, and therefore more reactive, states, but it is also possible that the higher temperature increases the average atomic kinetic energy, especially for the Na beam which is not as well collimated as the Ba beam. This added kinetic energy could then drive the endothermic reaction from the 15d and 16d states.

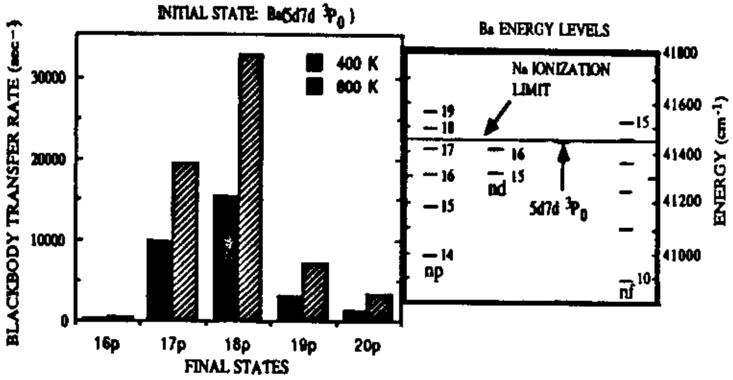
While it is difficult to separate the effects of blackbody induced state changing from those of increased kinetic energy for the pure Rydberg 15d and 16d states, the situation at the perturbed 5d7d $^3P_0$ state is more certain. Recall that this state is only ~7 cm^{-1} below the threshold energy for ionization of the Na atoms. Further, the lower temperature spectrum shows that this state is essentially unreactive. We can however transfer this state to a pure Rydberg state by blackbody induced transfer.

The matrix element that is needed to compute A_{if}, the Einstein coefficient that is needed to compute the blackbody induced transfer rate, K_{if}, is of the form

$$<\Psi_i|p|\Psi_f> = <\alpha\phi_{18s} + \beta\phi_{5d7d}|p|\phi_R>$$

where we have used the fact that the Rydberg character of the perturbed 5d7d $^3P_0$ state is 18s. The ϕ_R final state is a pure Rydberg np-state (recall the Laporte rule). Therefore, the second integral is very nearly zero, but blackbody radiation *can* excite the perturbed level to nearby p-states via the $<\alpha\phi_{18s}|p|\phi_{np}>$ contribution to the Einstein coefficient.

The results of the calculations are shown graphically.



Examination of the transfer out of the unreactive perturbed state and into the reactive Rydberg states illustrates the use of rate equations. We will therefore take this opportunity to examine this transfer using the following notation:

$N_P(t)$ = the time dependence of the density of atoms in the perturbed level.

$N_R(t)$ = the time dependence of the density of atoms in all Rydberg states to which transfer from the perturbed level can occur. These are Rydberg p-states.

K_T = total blackbody transfer rate out of the perturbed state

$k_{\ell\text{-mix}}$ = the ℓ-mixing rate constant

N_T = the total atom density

τ_R = average lifetimes of all the Rydberg p-states that result from the transfer

τ_P = lifetimes of the perturbed state (140 nsec)

$R = K_T + 1/\tau_P + k_{\ell\text{-mix}} N_T$

We make the following assumptions:

1. All accessible Rydberg states are reactive (even the lower lying 17p state).
2. $\tau_R >> \tau_P$. [$\tau_R \approx 16$ μsec & $\tau_p = 140$ nsec = 0.14 μsec]
3. τ_R is the average lifetime of all p-states to which transfer can occur.
4. There is no transfer back to the perturbed state.

The equations are:

a) $\frac{dN_P(t)}{dt} = -$ blackbody transfer rate − radiative decay − ℓ-mixing from the perturbed states

and

b) $\frac{dN_R(t)}{dt} = +$ blackbody transfer rate − radiative decay + ℓ-mixing from the perturbed states

or

a) $$\frac{dN_P(t)}{dt} = -K_T N_P(t) - \frac{1}{\tau_P}\cdot N_P(t) - [k_{\ell\text{-mix}} N_T]\cdot N_P(t)$$

b) $$\frac{dN_R(t)}{dt} = +K_T N_P(t) - \frac{1}{\tau_R}\cdot N_R(t) + [k_{\ell\text{-mix}} N_T]\cdot N_P(t)$$

Equation a) is easily solved:

$$N_P(t) = N_{P0}\exp[-(K_T + \frac{1}{\tau_P} + k_{\ell\text{-mix}} N_T)t]$$
$$= e^{-Rt}; \quad \text{where } R = (K_T + \frac{1}{\tau_P} + k_{\ell\text{-mix}} N_T)$$

Inserting this solution into b) we have

$$\frac{dN_R(t)}{dt} + \frac{1}{\tau_R} N_R(t) = [K_T + k_{\ell\text{-mix}} N_T] N_{P0} e^{-Rt}$$

The solution to this equation gives the desired quantity, the ratio of the density of pure Rydberg p-states to the initial density of the perturbed state:

$$\frac{N_R(t)}{N_{P0}} = [K_T + k_{\ell\text{-mix}} N_T]\cdot\frac{1}{\left[\frac{1}{\tau_R} - R\right]}\left\{\exp[-Rt] - \exp[-\frac{1}{\tau_R}]\right\}$$

Typical parameters are:

$K = 6.5 \times 10^4 \ \text{sec}^{-1}$

$k_{\ell\text{-mix}} N_T \approx 10^4 \ \text{sec}^{-1}$ [from $\sigma \approx 2 \times 10^4$ Å^2; $\bar{v} = 5 \times 10^4$ cm/sec and $N_T \approx 10^{11}$ cm^{-3}]

$\tau_R \approx 16$ μsec (p-states are longer-lived than d-states of the same n)

$\tau_P \approx 140$ nsec; therefore $[1/\tau_P] = 7.1 \times 10^6 \ \text{sec}^{-1}$

so $R = 7.1 \times 10^6 \ \text{sec}^{-1}$

We therefore have

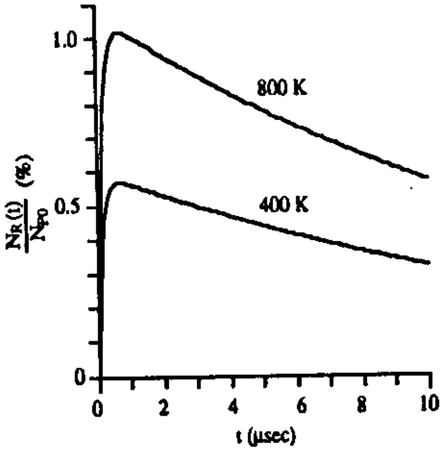
$$\frac{N_R(t)}{N_{P0}} = -1.07 \times 10^{-2}\left\{\exp[-7.1t] - \exp[-0.0625t]\right\}; \qquad \text{where t is now in μsec}$$

At 400 K the only change is in the pre-exponential factor which is -6×10^{-3}.

Now at a speed of ~10^5 cm/sec an atom will strike the walls ~1 cm away in about 10 μsec so that we need not consider times longer than this effective reaction time. The function above is zero initially and asymptotically, but we are interested only in the ratio for $0 < t < 10$ μsec.

$$\frac{N_R(t)}{N_{P0}} = -1.07[\exp(-7.1t) - \exp(-0.0625t)]$$
$$= -0.60[\exp(-7.1t) - \exp(-0.0625t)]$$

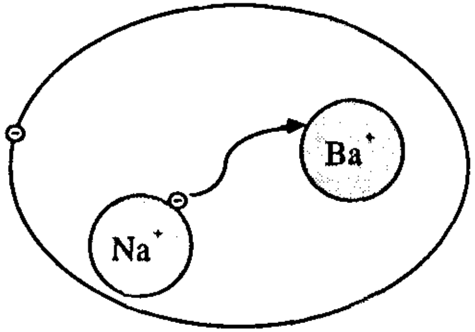
t is in μsec and $\frac{N_R(t)}{N_{P0}}$ in %



We see that at 800 K ~1% of the initial population of the 5d7d $^3P_0$ perturbed state is transferred to pure Rydberg p-states and that these Rydberg states last for the duration of effective reaction time.

We have so far ignored the fact that perturbed states are totally ineffective as reactants for Penning ionization. After all, these states do have a high fractional Rydberg component, $|\alpha|^2 \approx 0.4$ for the 5d7d $^3P_0$ perturbed state.

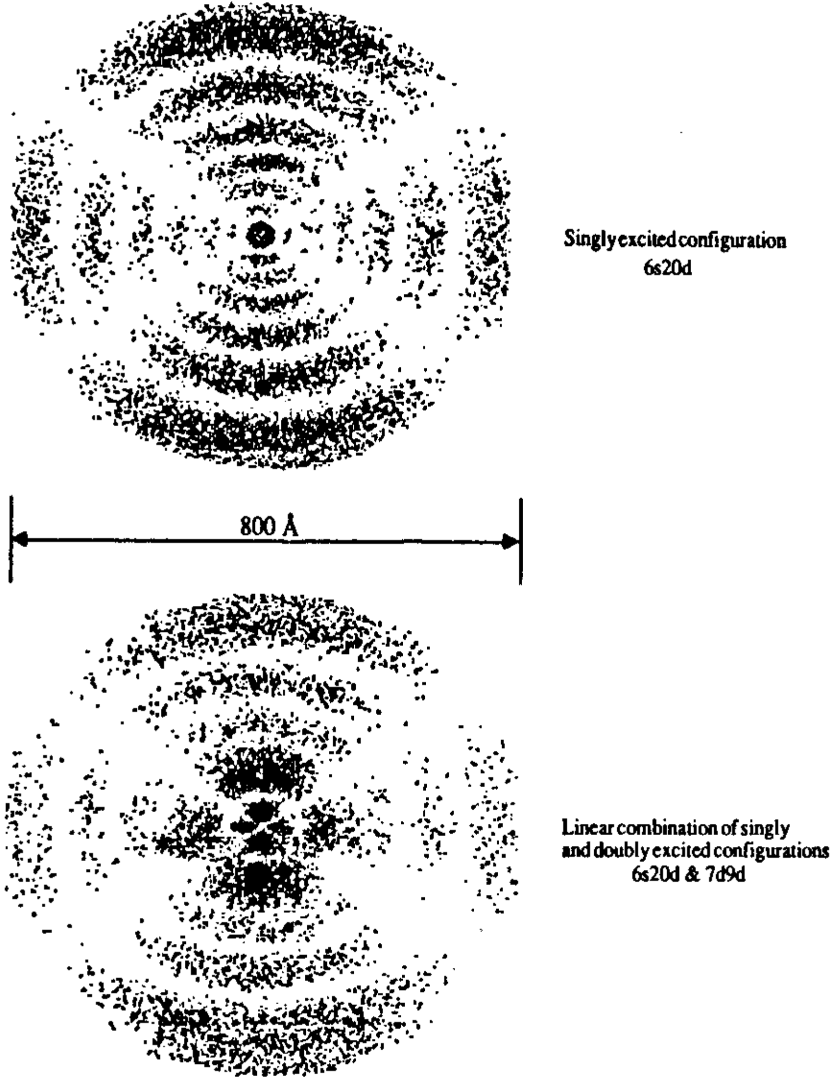
In an effort to explain this observation we consider a model in which the Penning ionization results from charge exchange between the Ba^+ core and the ground state Na atom *in the presence of the field of the Rydberg electron.* In this model the electric field of the Rydberg electron alters the energy levels of the quasimolecular ion-atom system to make the charge exchange a resonant process. Such processes are known to have higher cross sections than nonresonant ones.



PENNING IONIZATION WITH A PURE RYDBERG REACTANT STATE

In contrast to the pure Rydberg state depicted above, perturbed states have a greater concentration of the electronic charge close to the Ba^{++} (Xe-like) core so that perturbation of the quasimolecular levels can occur only at much shorter range than for pure Rydberg states. If this model is valid then the cross section for Penning ionization by pure Rydberg states should be considerably larger than Penning ionization by a perturbed state simply because of the spatial extent of the atoms. By spatial extent we mean the extent of the electron probability distribution as shown on the next page. (Note that the cross section must however not be greater than the geometric cross section.)

EXCITED STATE ELECTRON DISTRIBUTIONS FOR BARIUM



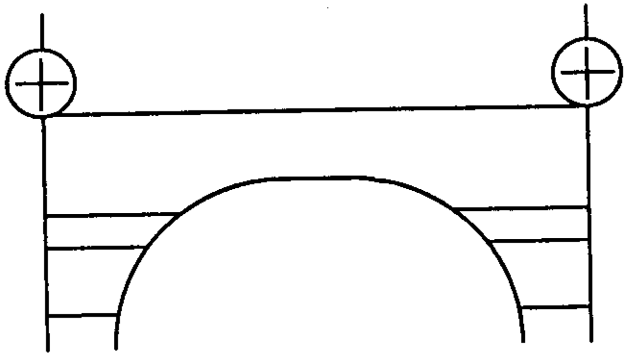
Singly excited configuration
6s20d

Linear combination of singly and doubly excited configurations
6s20d & 7d9d

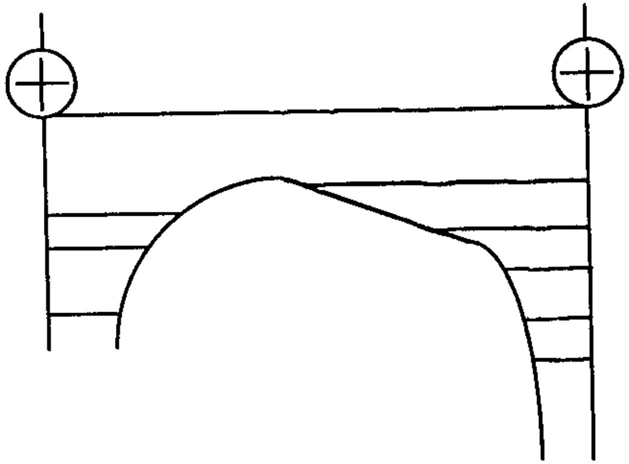
Comparison of the electron distributions for a pure Rydberg state (6s20d) and a mixed Rydberg-valence state (7d9d and 6s20d). The darkest regions are regions of the highest electron probabilities. The 7d9d configuration was chosen rather than the 5d7d for the purpose of illustration. That is, the 5d7d distribution is too compact to show up well on the diagram.

Electron distributions courtesy of C. E. Burkhardt, University of Missouri - St. Louis

SYMMETRIC CHARGE TRANSFER



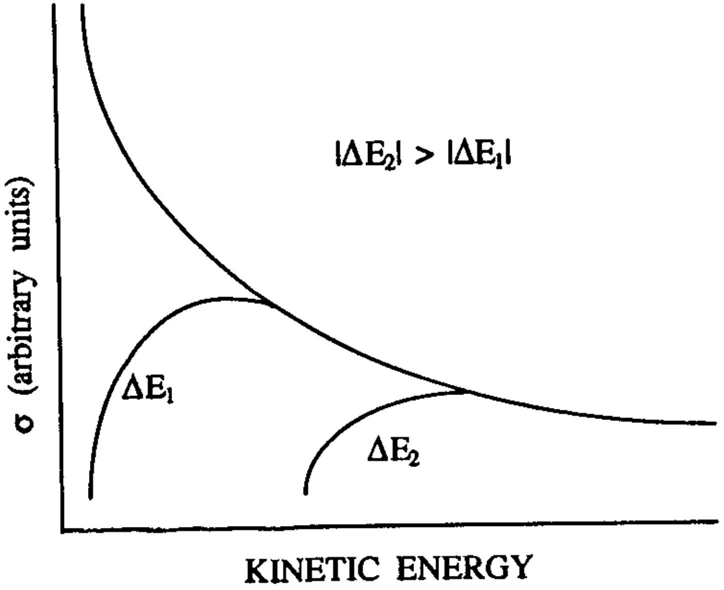
ASYMMETRIC CHARGE TRANSFER



In symmetric charge transfer, that is $X^+ + X \rightarrow X + X^+$, the electron may readily tunnel from one ionic core to the other leading to a probability of 1/2 of finding it on either. We may view the Rydberg electron as providing a field that shifts the energy levels for $X^+ + Y$ charge transfer "into resonance".

The graph below shows how the cross section behaves for several different values of the difference of the ionization potentials.

CROSS SECTION VS. KINETIC ENERGY FOR CHARGE TRANSFER



In our discussions we have tried to emphasize the following points:

1. Rydberg atoms have extreme properties which make it possible to study ordinary atoms using Rydberg atoms as "amplifiers" of these properties.

2. Care must be taken when using Rydberg atoms to probe atomic properties because the extreme properties that are so useful can be a two-edged sword. In particular, the state-selectivity provided by laser excitation can be rapidly destroyed by the huge ℓ-mixing cross sections or the extreme sensitivity to blackbody radiation.

3. The use of highly excited barium atoms gives us an opportunity to contrast the properties of pure Rydberg states with those of highly perturbed levels, the latter being very different in nature from the Rydberg states.

Along the way however we have attempted to review (or at least outline) the physical principles necessary for understanding.