Ramped Pulse Field Ionization Rydberg Spectroscopy of RaF

Transition Detection Is Exclusively via Ionization of RaF

Need to Design Experiments that Simultaneously Ask Multiple Questions

RaF is spectroscopically very similar to BaF

Every experimental scheme can be tested on BaF

For BaF the Ionization Threshold Lies Below the Dissociation Energy:

Unusual and convenient but: Is It true for all Actinide Monofluorides?

The Rydberg Equation: IP-$E_{n*\ell}$= $RZ^2/n*^2$

- n* is the effective principal quantum number
- n*≡n-$\delta_{\ell\lambda}$ $\delta_{\ell\lambda}$ is the "quantum defect"
- It turns out that we can borrow almost everything from the H atom
  - Formulas for energy levels and matrix elements
- Rydberg series, each series built on a shape invariant innermost $\ell\lambda$ orbital lobe with amplitude scaled as n*$^{-3/2}$

Hydrogen Atom Scaling Rules   T. Gallagher   Rydberg Atoms

Table 2.3. *Expectation values of r^σ for H.*[a]

$$\langle r \rangle = \frac{1}{2}[3n^2 - \ell(\ell+1)]$$ radius, dipole transition moment

$$\langle r^2 \rangle = \frac{n^2}{2}[5n^2 + 1 - 3\ell(\ell+1)]$$

$$\langle 1/r \rangle = 1/n^2$$

$$\langle 1/r^2 \rangle = \frac{1}{n^3(\ell+1/2)}$$ centrifugal barrier

$$\langle 1/r^3 \rangle = \frac{1}{n^3(\ell+1)(\ell+1/2)\ell}$$ spin-orbit

$$\langle 1/r^4 \rangle = \frac{3n^2 - \ell(\ell+1)}{2n^5(\ell+3/2)(\ell+1)(\ell+1/2)\ell(\ell-1/2)}$$

$$\langle 1/r^6 \rangle = \frac{35n^4 - 5n^2[6\ell(\ell+1) - 5] + 3(\ell+2)(\ell+1)\ell(\ell-1)}{8n^7(\ell+5/2)(\ell+2)(\ell+3/2)(\ell+1)(\ell+1/2)\ell(\ell-1/2)(\ell-1)(\ell-3/2)}$$

[a](from refs. 2, 11)

Table 2.4. *Properties of Rydberg atoms.*[a]

Property	n dependence	Na(10d)
Binding energy	n^{-2}	0.14 eV
Energy between adjacent n states	n^{-3}	0.023 eV
Orbital radius	n^2	147 a_0
Geometric cross section	n^4	68 000 a_0^2
Dipole moment $\langle nd|er|nf \rangle$	n^2	143 ea_0
Polarizability	n^7	0.21 MHz cm^2/V^2
Radiative lifetime	n^3	1.0 μs
Fine-structure interval	n^{-3}	−92 MHz

[a](from ref. 1)

Experimental Sequence for RaF

- The approximate IP gives a map of Rydberg State Space
  - Energy levels: $n*$ to $n*+1$ scaling of all members of a Rydberg series
  - $n*$-scaling of all matrix elements, $n*$ to $n*'$ transition moments scale as $(n*n*')^{-3/2}$
- Each $n*$, $n*+1$ energy interval contains one member of each Rydberg series, and everything scales as $(n*+ \frac{1}{2})^{-3}$
- Core-Nonpenetrating ($\ell>3$) Rydberg States have near-integer $n*$ values, which means that you know *a priori* an $\Re/n^2$ ladder of energy level spacings. This enables you to convert a simple laser or mm-wave frequency scan into a double resonance experiment.
- Core-nonpenetrating Rydberg states are extremely sensitive to electric field, core-penetrating Rydberg states less so.
- After every laser pulse, ramped pulse field ionization provides n-assignments.
- In every experiment, the value of the IP is refined. This means that all frequency scans can be narrower, higher resolution, and richer in information.
- Sub-MHz precision is possible in a ramped pulsed field ionization-detected chirped pulse mm-wave spectrum. [F. Merkt]

How far do we need to scan?XXXX

- Core Penetrating States
  - Tunable laser near 1000 cm^{-1}
    - $5 < n^* < 6 \, \Delta\nu/cm^{-1}$

6.00	800
5.53	1000
5.02	1300

  - Millimeter-Wave near 100 GHz

n^*	
39.92	99 GHz
39.01	106 GHz

  - Binding energy at $n^* = 39.5$ 70.3 cm^{-1}
- Core Nonpenetrating States: $n^* = 40.0 + 0.05$,
  - Binding Energy 69 cm^{-1}

40.55	-2007.5 GHz
40.45	-2010.6 3.20 GHz range

    Field Ionization: $V/cm^{-1} = 6.12 \, [F/V/cm]^{1/2}$ 120 V/cm is required

EDIT Basis for n*-Scaling in Rydberg-Land

- Every property of H atom scales as an explicit function of n and ℓ
  - for example $IP - E_{n\ell} = \mathfrak{R}/n^2$ $\mathfrak{R}$ is the mass-dependent Rydberg Constant, $E_{\infty\ell} = IP$ for n= ∞
- Same for *one-electron* atomic ions, but with an extra factor of nuclear charge, Z^2
- For *many-electron* atoms there is an ℓ-dependent departure from the hydrogenic formulas
  - We replace n by the *effective* principal quantum number, $n^* \equiv n - \delta_\ell$
  - δ_ℓ is the "quantum defect:" IT IS NOT A FUDGE FACTOR
  - It expresses how an electron in the ℓ orbital, partially shielded behind the $\hbar^2\ell(\ell+1)/\mu r^2$ centrifugal barrier, samples the nuclear charge.
  - There is no centrifugal barrier for an s orbital so the quantum defect for s orbitals is largest
    - $\delta_s > \delta_p > \delta_d, > \delta_f$ and all higher-ℓ orbitals have near-zero quantum defect: "non-penetrating"
    - The quantum defects are independent of n!

For Molecules, One Needs Multichannel Quantum Defect Theory, MQDT, Expressed As a Matrix Equation

- When n* is an integer the "regular Coulomb functions" go to zero as $r \to \infty$

- When n* is integer the Rydberg series is core non-penetrating (CNP), when n* is non-integer the Rydberg series is core-penetrating (CP)

- CNP and CP series respond very differently to an external electric field

- When n* is not an integer, the members of each λ-eigen-channel are a n*-independent linear combination of ℓ basis functions, constructed so that all members of that channel go to zero as $r \to \infty$.

- For BaF, s, p, d, and f channels are core-penetrating. There are 10 eigenchannels for + Kronig symmetry: 4 σ, 3 π, 2 δ, and 1φ, and six eigenchannels for – Kronig symmetry, 3 π, 2 δ, and 1 φ.

EDITWhat is Going On Here?

- The shape of the inner-most lobe the infinite number of members of an nℓ Rydberg series
- All n-members of a Rydberg series of nℓ orbitals have the same shape, but their amplitude scales as n*$^{-3/2}$
- This is the basis for all n*-scaling in Rydberg land
- $2\pi\delta_\ell$ is the phase shift for the nℓ orbital of a many-electron atom relative to that for the corresponding H atom nℓ orbital.
- The Rydberg electron on a many-electron atom sees Z^{eff}>1, which means it accumulates extra phase in its collision with the nucleus.
- The lowest energy member of each Rydberg is the "terminus state".

The Rydberg Equation

- IP - $E_{n*\ell} = \mathfrak{R}/n*^2$ The zero of energy is the energy of the ground state
- $n* = [\mathfrak{R}/(IP - E_{n*\ell})]^{1/2}$
- The energy difference between the n* and n*+1 states in the nℓ series is

  $E_{n*+1} - E_{n*} = 2\mathfrak{R}/(n*+1/2)^3$

- Similarly, the energy difference between the n*ℓ and n*'ℓ' states is

  $E_{n*\ell} - E_{n*'\ell'} = 2\mathfrak{R} \; (n*'-n*)/[(n*+n*')/2]^3$

- All n*, n*' matrix elements scale as $(n*n*')^{-3/2}$

Special Stuff

- State space is organized according to *a priori* known rules
- $\Delta v=0$ propensity rule for Rydberg-Rydberg transitions
- Electric Field Effects: huge difference between behavior of core-penetrating vs core non-penetrating
- ZEKE States: convergence of infinite Rydberg series on each rotation-vibration state of the ion: autoionization (slow)
- Pulsed field ionization: forced ionization (fast)
- Ramped pulsed field (F) ionization: $\Delta E/cm^{-1} \approx 6[F/V/cm]^{1/2}$
- Vibrational, rotational, and hyperfine structure of the cation
- Two-question experiments

Ideas for Experiments

ns Rydberg states are special because they have large and $n^{*-3/2}$ amplitude scaled s-character inside the nucleus

Is IP$<$D^0 Predissociation causes breakdown of all rules and expectations

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