# CaF: Just Large Enough, and Ca: Even Smaller

Robert W. Field

Massachusetts Institute of Technology

12 November 2010

# Outline

- Goals
  - Global model: all spectra, all dynamics
  - Core-nonpenetrating states: new state of matter
- Experimental Methods
  - REMPI vs. direct FID detection
- Fits to Massively Perturbed Spectra
  - Multichannel Quantum Defect Theory
- Zone of Death
  - Predissociation and autoionization
- Free Induction Decay Signal: 5 kilo-Debye
  - NMR-esque tricks

# Why CaF?

Simplest chemically-relevant “not-atom”

Like Na

1 $e^-$ outside closed-shell ion-core

Unlike $Na^+$

* $(Ca^{2+})(F^-)$ is *profoundly* not round
* Not-roundness is R,E-dependent

Mechanisms for $e^- \leftrightarrow$ nuclei energy exchange

**CHEMISTRY!**

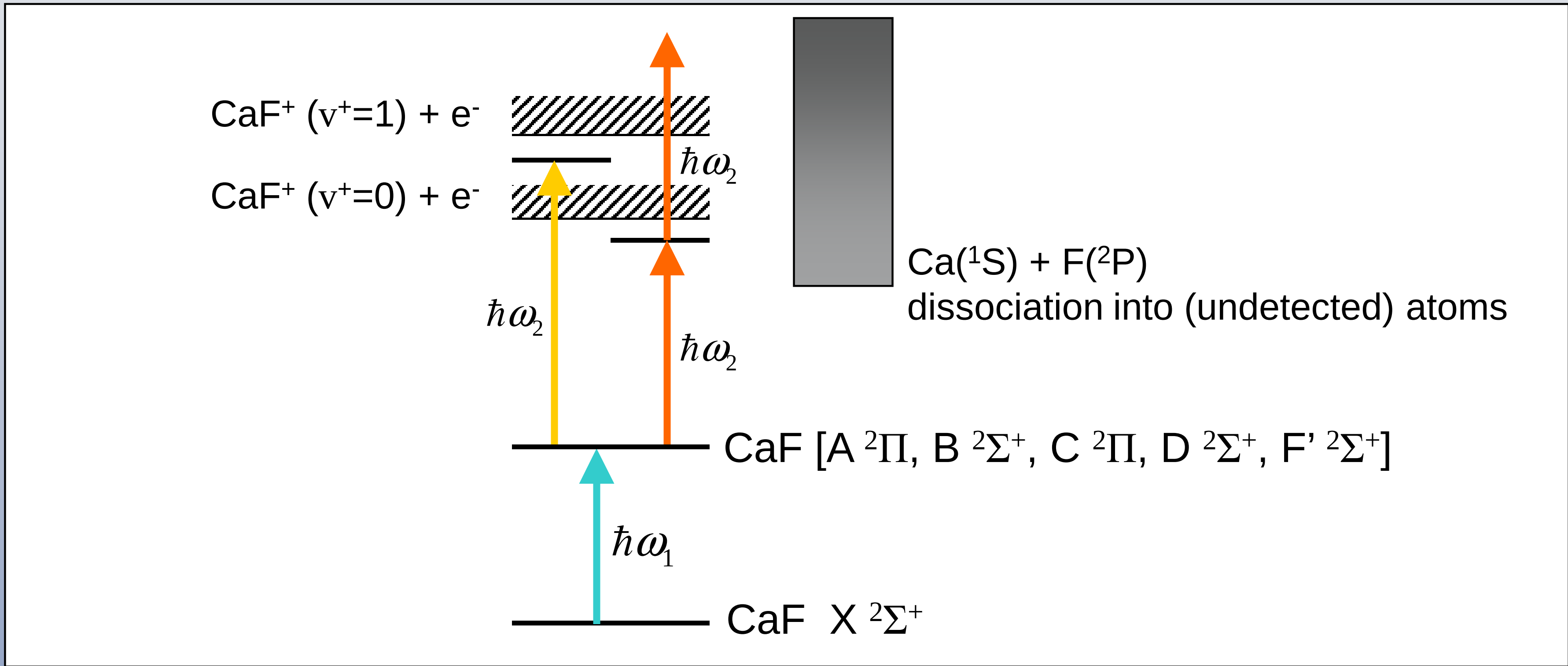
# Why Ca?

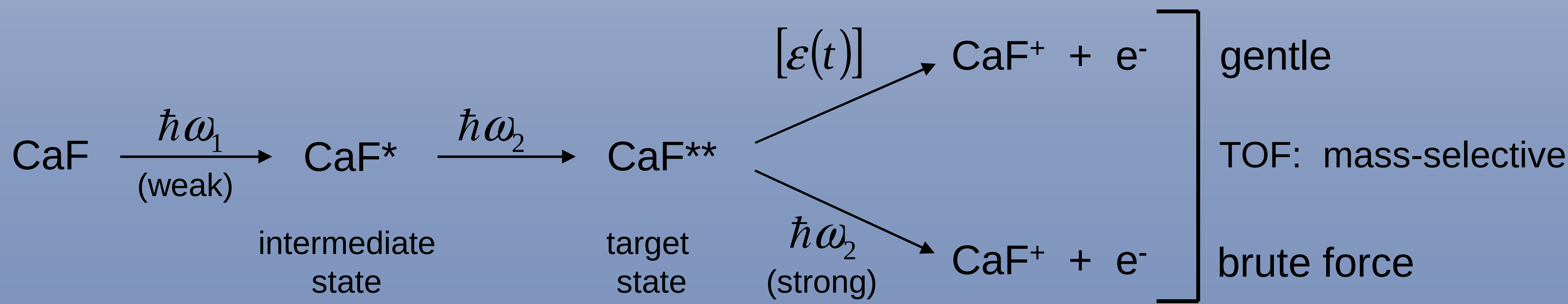
- Experimentally a little easier than CaF
- Pulsed photo-ablation supersonic jet source, as for CaF
- Free Induction Decay (FID) detection of electronic transitions in an atomic beam!
- NOT detected by ion, $e^-$, or optical photon!
- $10^4$ resolution elements in single shot, meaningful relative intensities (like NMR)
- $10^3$ times better resolution than dye laser

# Experimental Methods

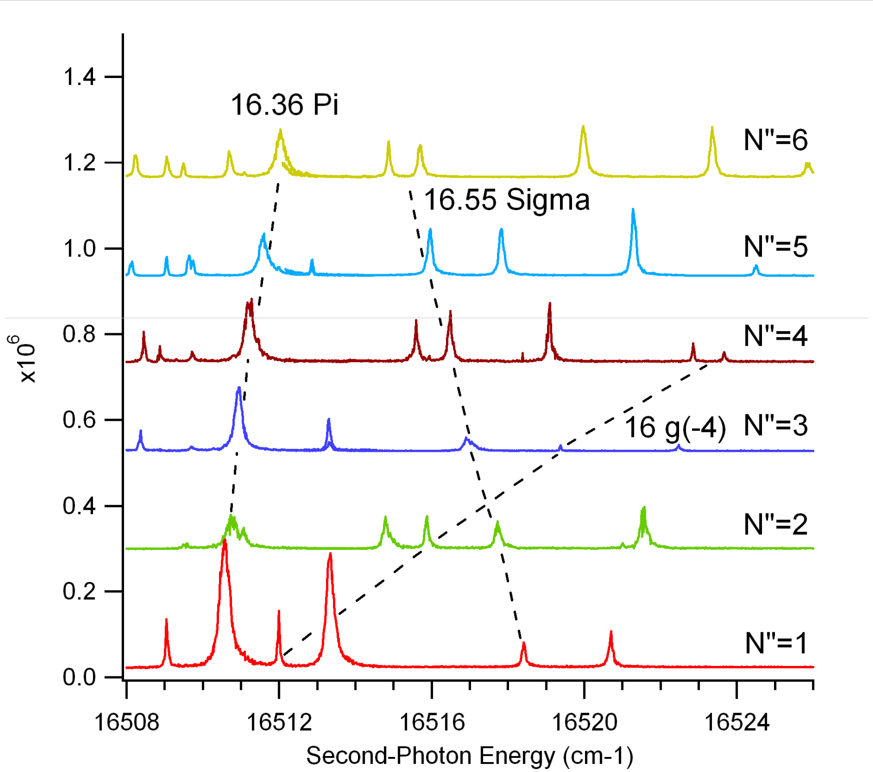
- Rydberg-Rydberg transitions in a supersonic molecular beam with a photoablation source of atoms/molecules
- 2 Color laser excitation to Rydberg states
- Resonance Enhanced Multiphoton Ionization (REMPI) *indirect* detection
  - 0.04 $cm^3$ active volume
  - Must use very low laser pulse energy
- Chirped Pulse mmW: *direct* detection of Free Induction Decay
  - 100 $cm^3$ active volume: $10^8$ Rydberg Atoms, 5 kDebye transition moments
  - Can use maximum laser pulse energy

# CaF Experimental Schemes

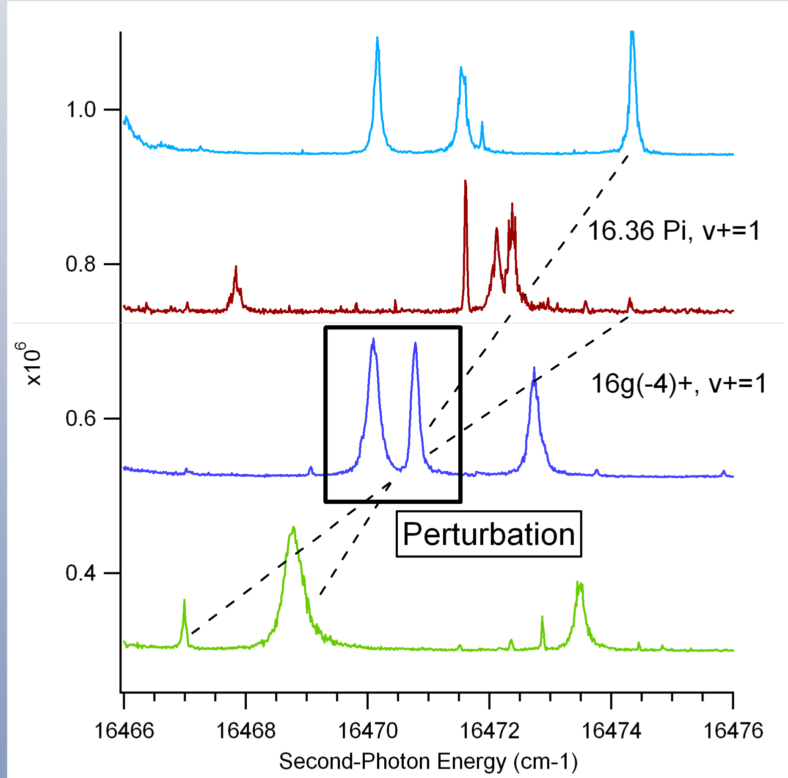


# Linewidths, Perturbations, Stacked Plots

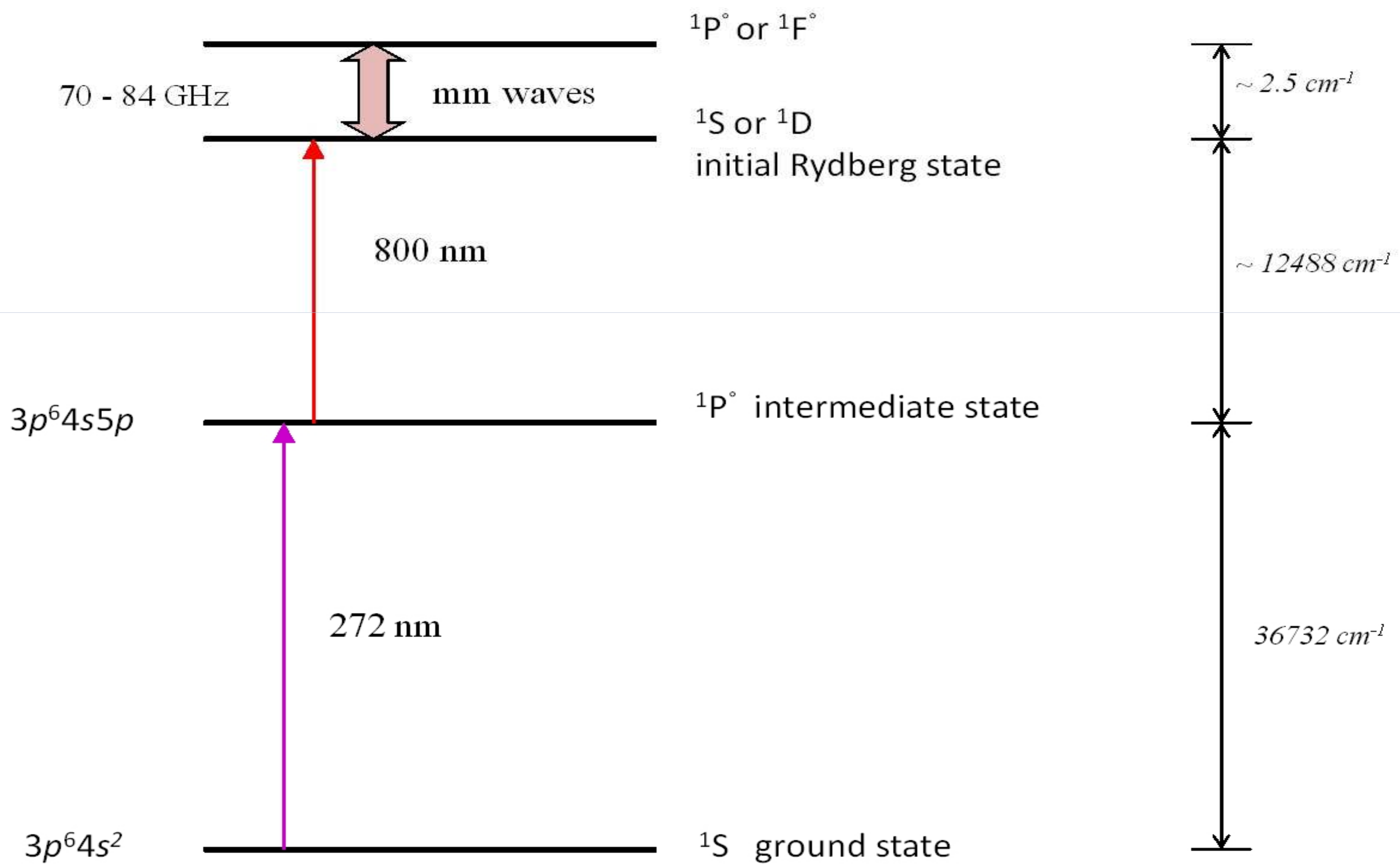



Some broad and some narrow lines

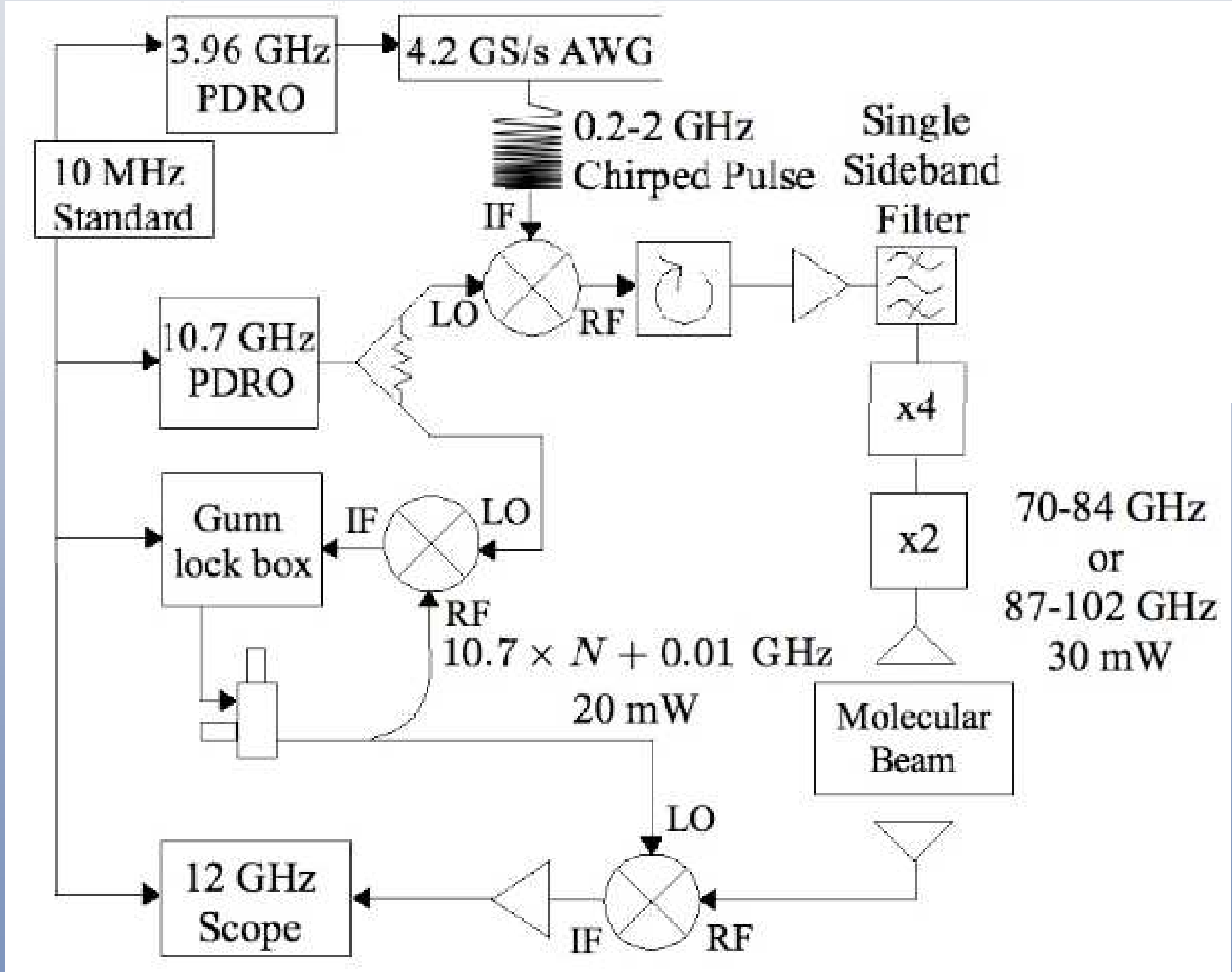



Intensity *and* linewidth sharing at a strong perturbation

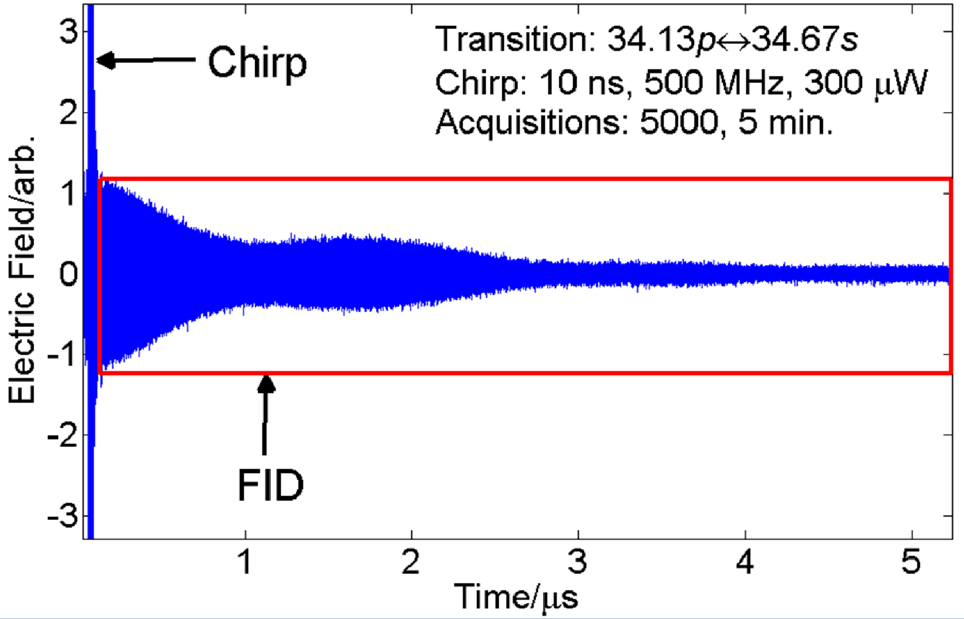
# Level Diagram for mm-Detected Optical-Optical-mm Triple Resonance

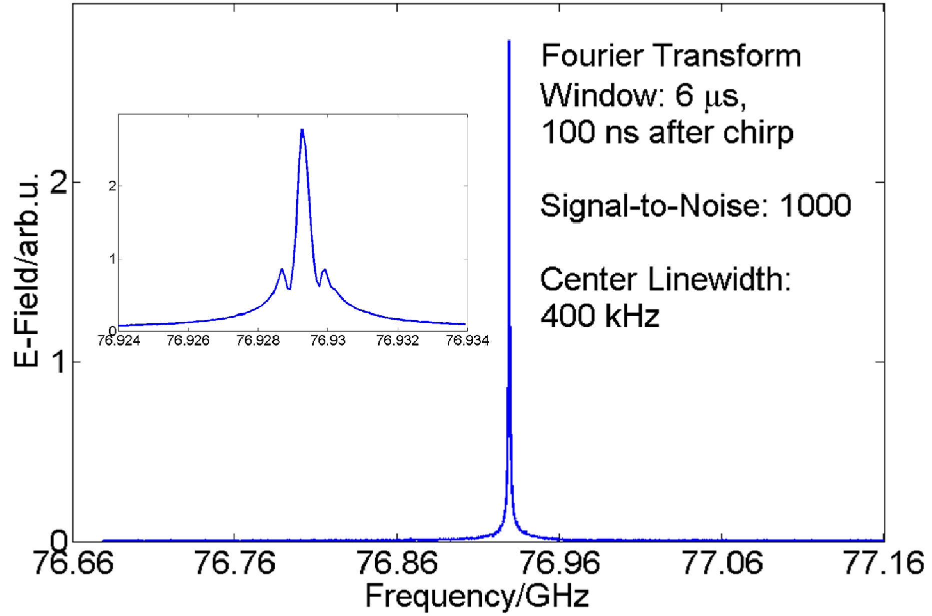


# Chirp Generation, FID Detection
# á la Brooks Pate



# Our First Rydberg-Rydberg FID: Zeeman Splitting not Nulled



# Rydberg Equation

$E_{n\alpha\lambda} = -\mathcal{R}/(n- \mu_{\alpha\lambda})^2 = - \mathcal{R}/n^{*2}$

$n^*$ is the effective principal quantum number for the mixed-$\ell$ α,λ Rydberg series, $\mathcal{R}$ is the Rydberg constant.

$\mu_{\langle\lambda}$ is the eigen-quantum defect. Not a fudge factor! It is an eigenvalue of μ(R,E). $\pi\mu_{\langle\lambda}$ is a phase shift.

μ(*R*,*E*) is the quantum defect matrix

Strongly *R*-dependent
Weakly *E*-dependent

**Describes all spectra and all dynamics**

**We have experimentally determined all of the elements of the μ,** d**μ**/dR**, and** d**μ**/E **matrices.**

# Completeness of States Characterized: s~p~d~f
# Core-Penetrating **Supercomplexes**
# Plus f, g, and h **Nonpenetrating** States

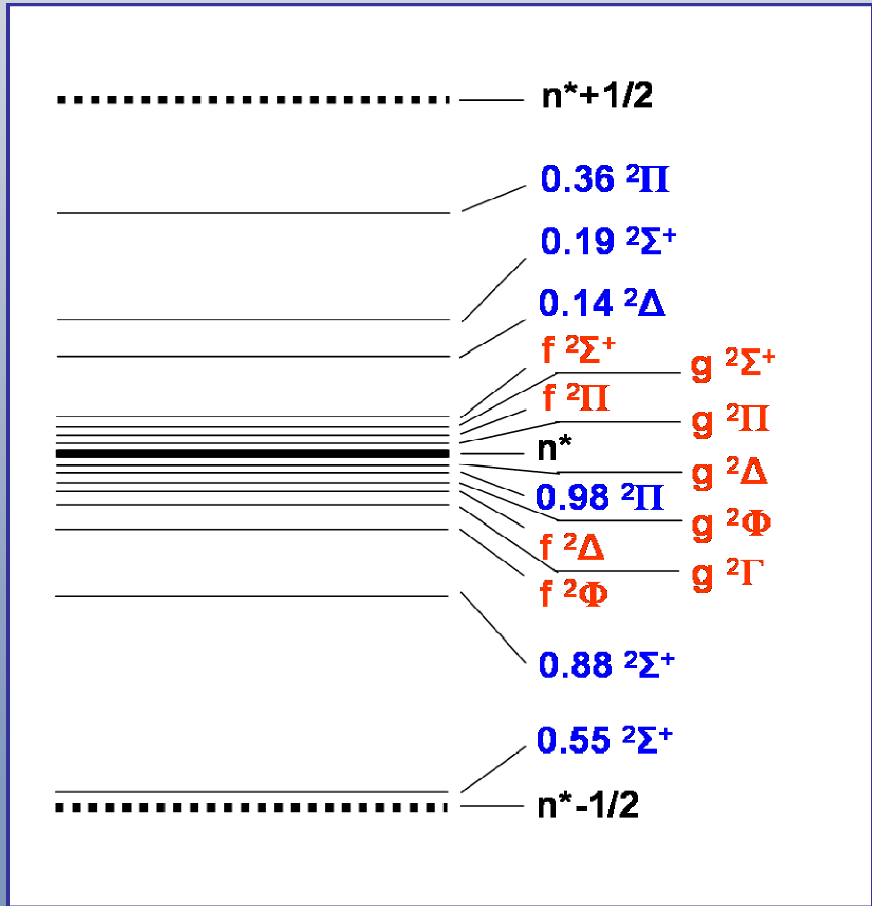
## Eigenquantum Defects

| | s | p | d | f |
|---|---|---|---|---|
| Σ | 0.46 | 0.12 | -0.18 | -0.06 |
| Π | | -0.35 | -0.04 | -0.03 |
| Δ | | | -0.12 | 0.03 |
| Φ | | | | 0.1 |

## Partial-$\ell$ Characters

| | %s | %p | %d | %f |
|---|---|---|---|---|
| s Σ | 85 | 14 | 1 | 1 |
| p Σ | 13 | 85 | 0 | 3 |
| p Π | | 59 | 38 | 2 |
| d Σ | 3 | 0 | 56 | 41 |
| d Π | | 40 | 50 | 10 |
| d Δ | | | 96 | 5 |
| f Σ | 0 | 2 | 42 | 56 |
| f Π | | 1 | 11 | 88 |
| f Δ | | | 5 | 96 |
| f Φ | | | | 100 |

## Scaled Energy Level Pattern:
## **n* Template**



# Two Flavors of Rydberg States

- Core-Nonpenetrating: long range probe of ion-core multipole moments (μ,Q,O) and polarizability (α,γ)
  - Huge $|\Delta n^*|<1$ transition moments, long lifetimes
  - Inside-out ligand field theory
  - Algebraic formulas: splittings→μ,Q,O,α,γ of ion
    - J. Chem. Phys. 128, 194301, (2008).
- Core-Penetrating: hard collisions of $e^-$ with ion-core
  - Series terminus state encodes intra-core dynamics

# Penetrating vs. Nonpenetrating Rydberg Orbitals

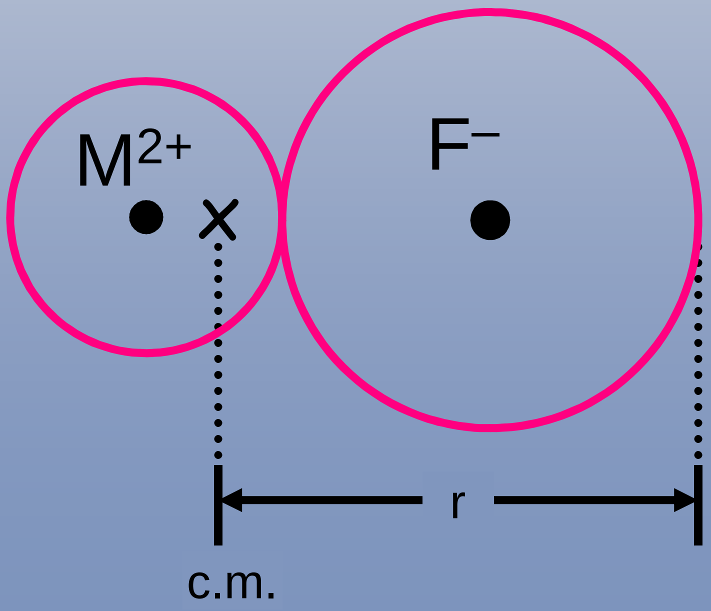
$$V_\ell(r) = -\frac{Z^{\text{eff}}(r)}{r} + \frac{\ell(\ell+1)}{2m_e r^2}$$

turning points

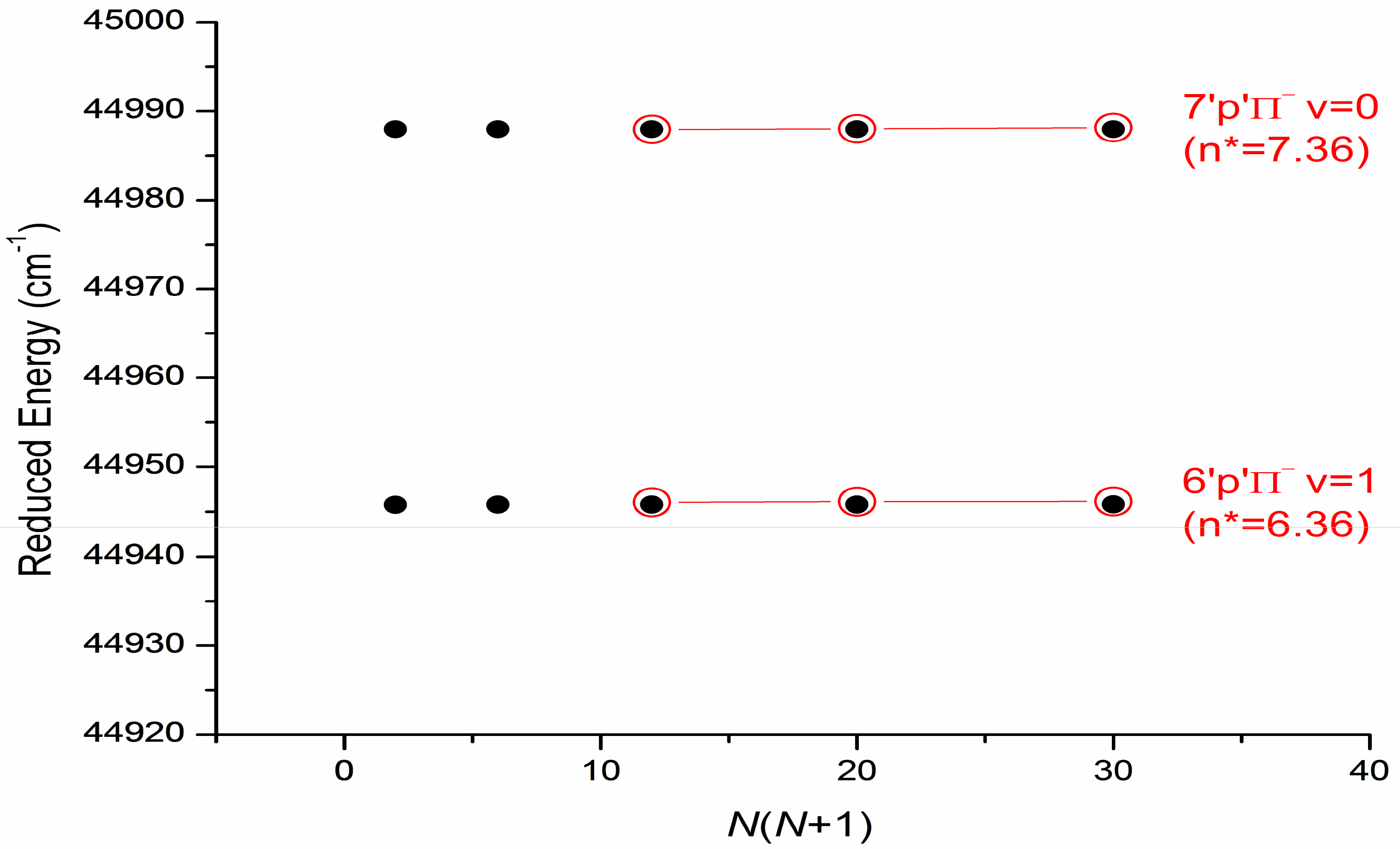
$$V_\ell(r_\pm) = E_{n\ell} = -\Re c / n^2$$

$$r_\pm = n^2\left[1 \pm \left(1 - \frac{\ell(\ell+1)}{n^2}\right)^{1/2}\right] \quad \text{a.u.}$$

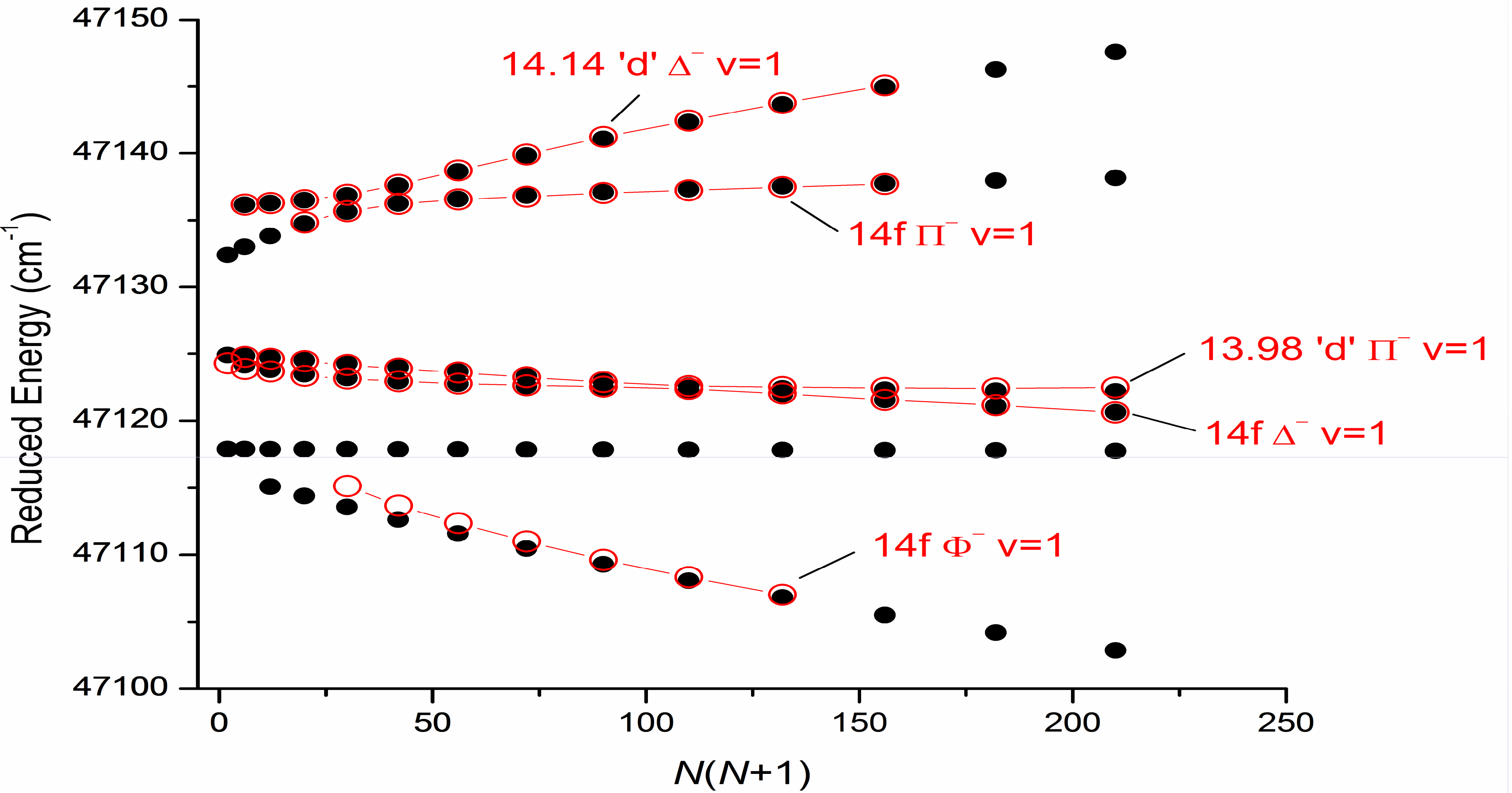
| | $r_-/\text{Å}$ | $r_+/\text{Å}$ |
|---|---|---|
| 2p | 0.62 | 3.61 |
| 3d | 2.06 | 7.51 |
| 4f | 4.23 | 12.70 |
| 5g | 7.32 | 19.14 |



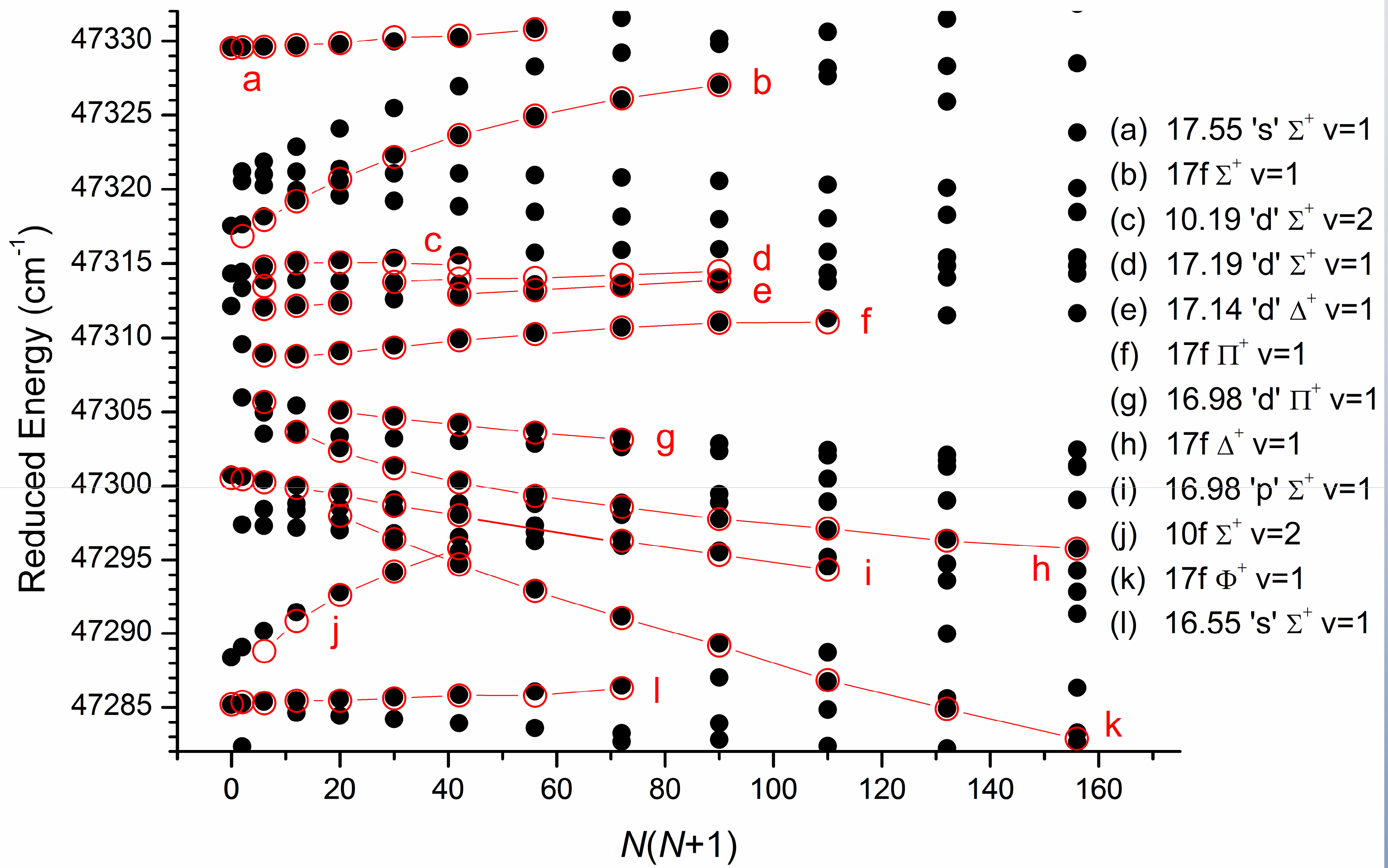

2.70 Å for $CaF^+$
f should be nonpenetrating




Example of a strong $\Delta v^+=1$ perturbation. In the absence of the perturbation, the 7.36 'p' $\Pi$ v=0 and 6.36 'p' $\Pi$ v=1 levels are nearly degenerate. The perturbation causes a ~45 cm$^{-1}$ splitting of the levels and complete mixing of the wavefunctions. This same mechanism causes vibrational autoionization.




Quality of fit in the 14f complex. A rotational perturbation between the 14f $\Pi^-$ and the 14.14 ‘d’ $\Delta^-$ interloper state gives rise to the avoided crossing at the top of the figure.




Quality of fit in the n* = 16.5 – 17.5 region. Above n* ≈ 16, rotational interactions are strong and ubiquitous.

# A Complete Model? (1)

$$\mu^{(N,\lambda,parity)}(R,E) = \mu(R_e^+, E=0) + \frac{\partial\mu}{\partial R}(R - R_e^+) + \frac{\partial\mu}{\partial E} E$$

**ALL ENERGY LEVEL SPLITTINGS** $E_{n^*+\delta/2} - E_{n^*-\delta/2} = \dfrac{2c\Re\delta}{n^{*3}}$

**ALL OFF-DIAGONAL MATRIX ELEMENTS OF EVERYTHING**

$$\langle n^* | \mathbf{A} | n^{*\prime} \rangle = A_0 \left( n^* n^{*\prime} \right)^{-3/2}$$

$n^*$-scaling of $\omega_{e,n^*}$, $B_{e,n^*}$, etc.

**ALL SPECTRA**

**ALL DYNAMICS**

**Once** $\mu\left(R_e^+\right)$ **,** $\left.\dfrac{\partial\mu}{\partial R}\right|_{R_e^+}$, and $\left.\dfrac{\partial\mu}{\partial E}\right|_{R_e^+}$ **are determined, the picture is complete.**

# A Complete Model? (2)

$$\mu^{(N,\lambda,parity)}(R,E) = \mu(R_e^+, E=0) + \frac{\partial\mu}{\partial R}(R - R_e^+) + \frac{\partial\mu}{\partial E}E$$

**ALL ENERGY LEVEL SPLITTINGS** $E_{n^*+\delta/2} - E_{n^*-\delta/2} = \dfrac{2c\Re\delta}{n^{*3}}$

**ALL OFF-DIAGONAL MATRIX ELEMENTS OF EVERYTHING**

$$\langle n^* | \mathbf{A} | n^{*\prime} \rangle = A_0 \left( n^* n^{*\prime} \right)^{-3/2}$$

$n^*$-scaling of $\omega_{e,n^*}$, $B_{e,n^*}$, etc.

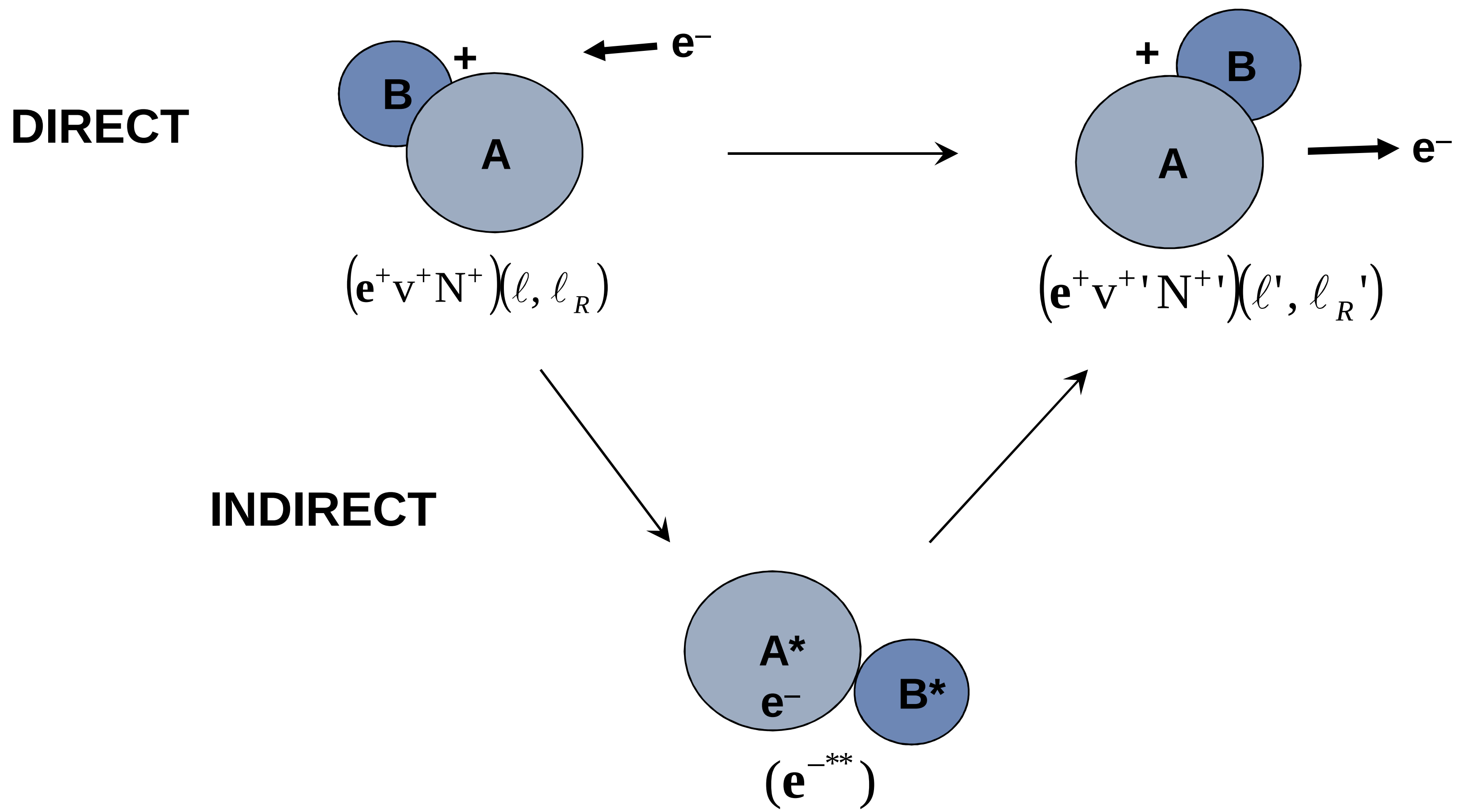
**ALL SPECTRA**

**ALL DYNAMICS**

**Once** $\mu\left(R_e^+\right)$, $\left.\dfrac{\partial\mu}{\partial R}\right|_{R_e^+}$, and $\left.\dfrac{\partial\mu}{\partial E}\right|_{R_e^+}$ **are determined, the picture is complete.**

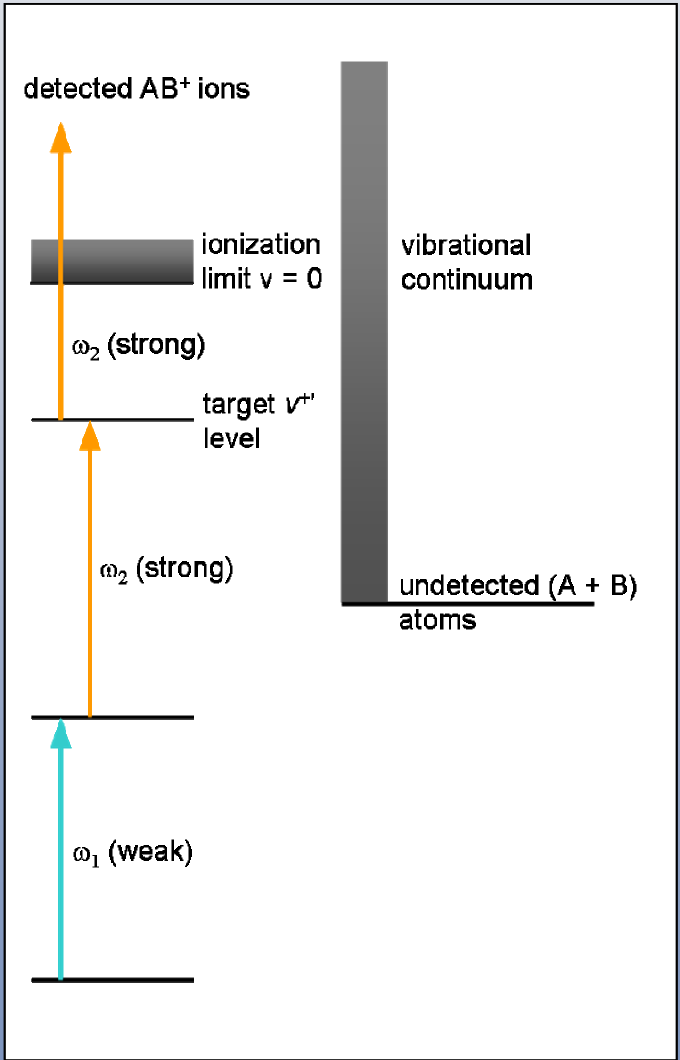
Or is it? **Presence of indirect processes!**

# Indirect Processes




**(AB⁺ + *e*⁻) Electronically Excited AB**

# Signatures of Indirect Processes




- $\Delta v^{+} = 0$ Franck-Condon propensity rule grossly violated
- (A+B) continuum ← intermediate
- $AB^{+}$ + $e^{-}$ ← (A+B) continuum

electronic transitions violate 1-$e^{-}$ selection rule

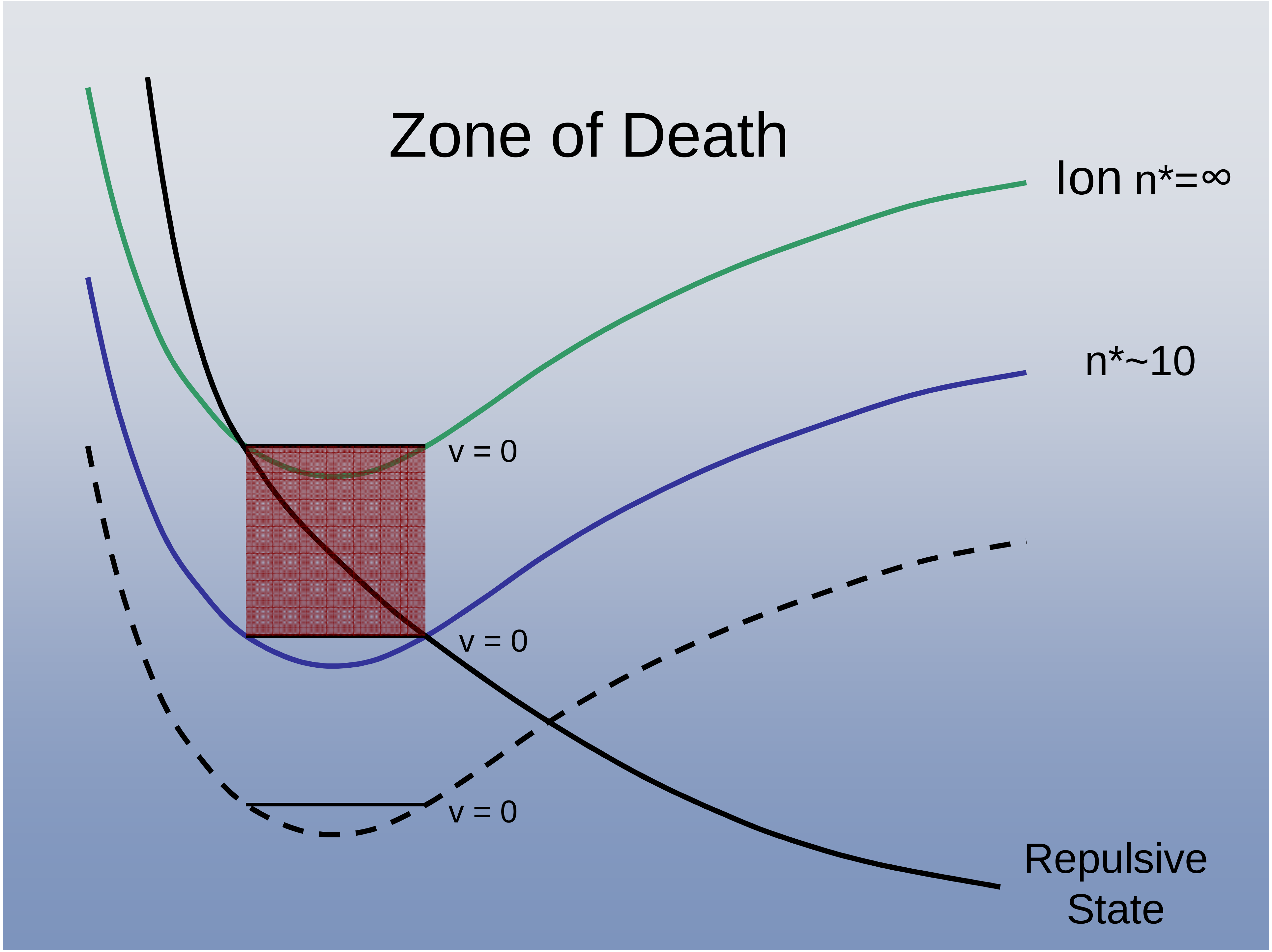
**Yet asymmetric (Fano) lineshapes**

- Quasi-continuous 2-photon non-resonant background overwhelms 2-step resonant sharp lines
- ($AB^{+}$ $v^{+}$, $N^{+}$) + ($e^{-}$ $\ell$, $\ell_R$ ) photofragments produced in states not consistent with μ(R)

**Every experimental observation seems to demand a special explanation**

**No big picture**

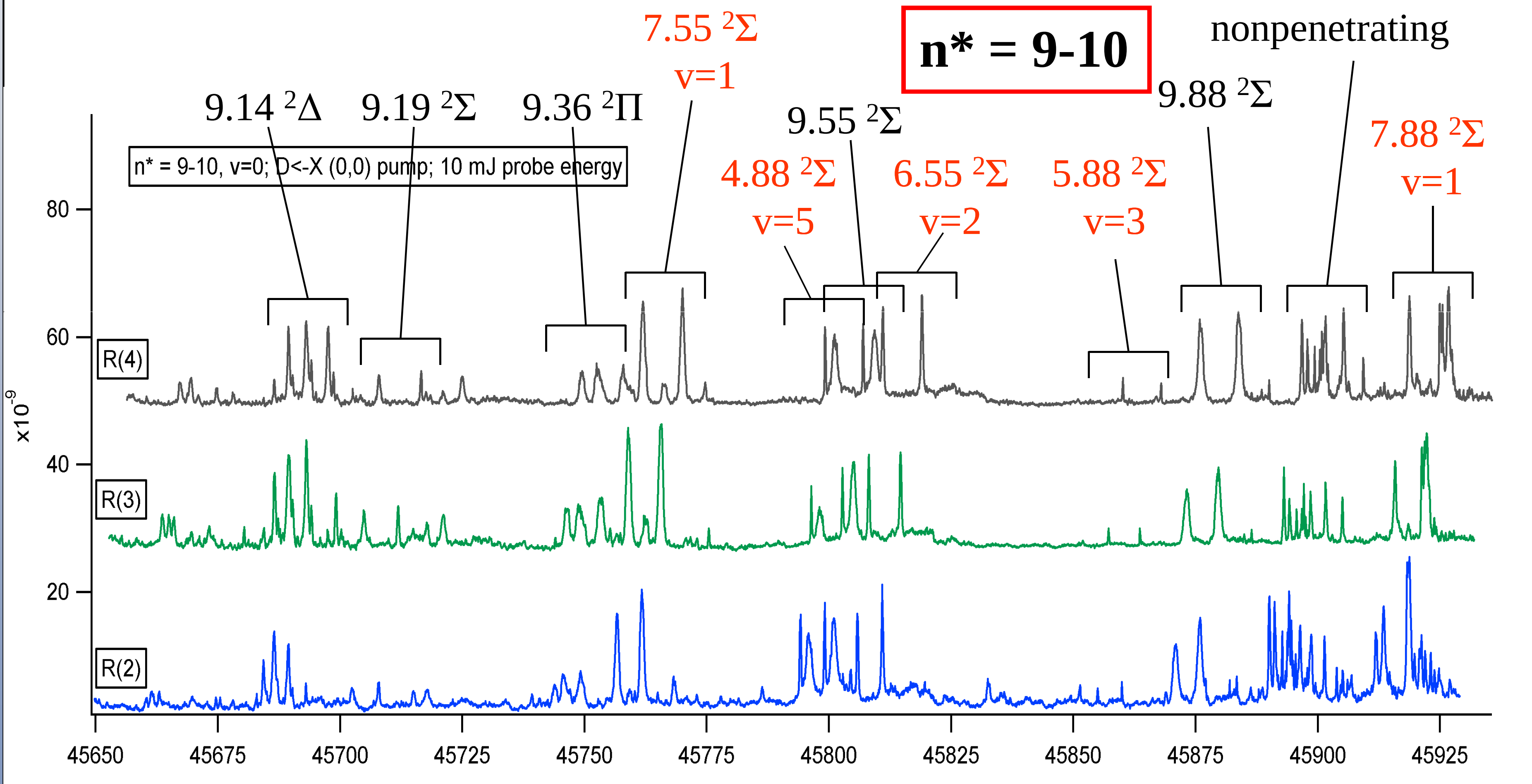
**But in CaF, all indirect processes are due to only one repulsive curve**


Zone of Death
Ion n*=∞
n*~10
v = 0
v = 0
v = 0
Repulsive State

# Zone of Death

- Short Lifetimes
  - Predissociation, Autoionization
  - Too short for FID detection
  - Too short for exotic applications
- Indirect Processes
  - One repulsive state shatters all propensity rules
- Rydberg Electron↔Ion-Core energy exchange: scales as $n^{*-3}$, $\sim\ell^{-10}$ (for $\ell>3$: Gallagher p. 410)
- Jump over the zone of death? High-$\ell$ states!
  - NMR-esque pulse gymnastics

# Spectra Grossly Violate Δv=0 Franck-Condon Propensity Rule




**Similar phenomena also observed in n* = 7-8, 8-9 regions**

# Observed Wrong-v Transitions Are Exclusively Σ

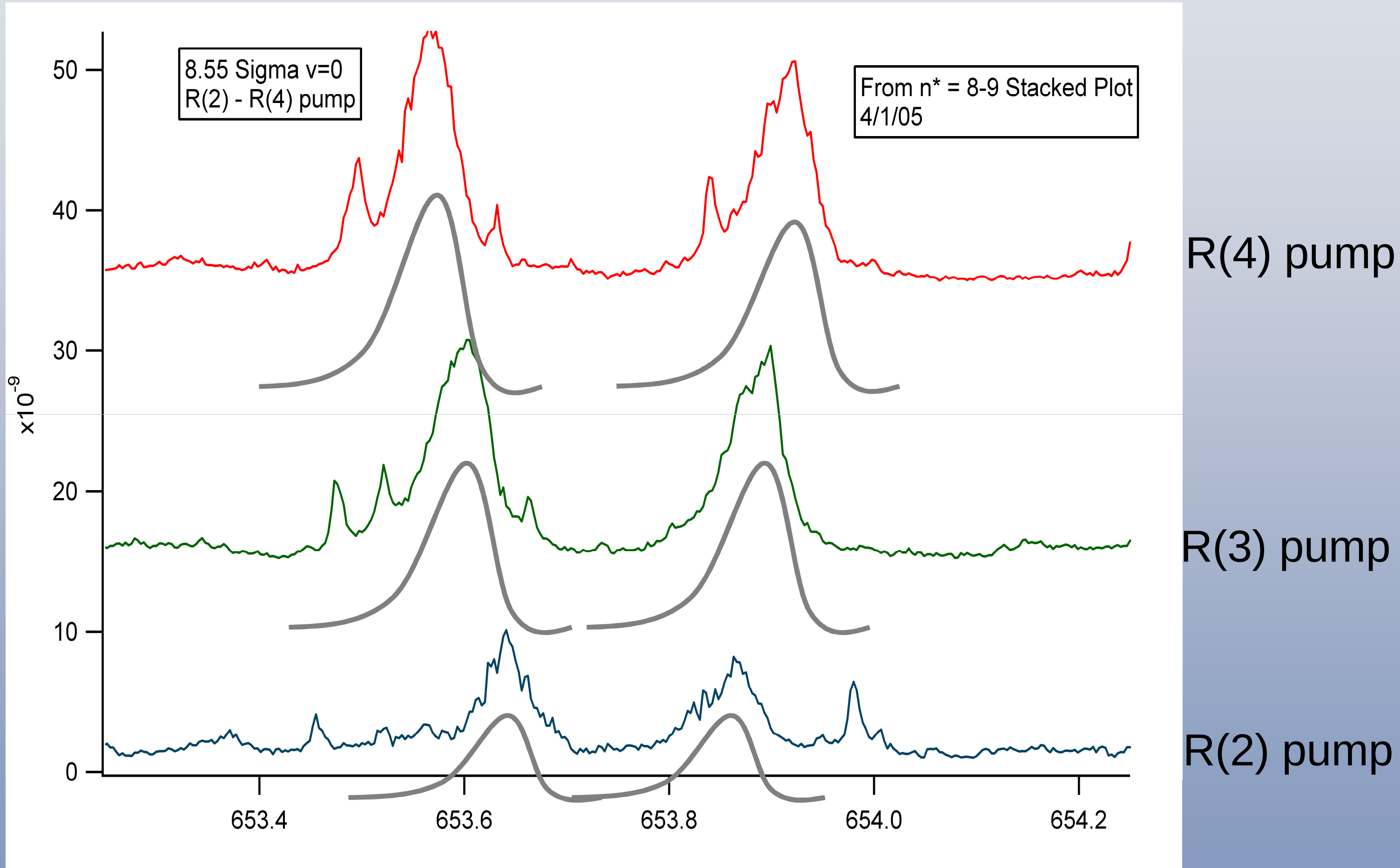
| v | Series | Symmetry | Observed? |
|---|---|---|---|
| 0 | 8.19 | Σ | ✓ |
| 0 | 8.36 | Π | ✓ |
| 0 | 8.55 | Σ | ✓ |
| 0 | 8.88 | Σ | ✓ |
| 0 | 8.98 | Π | ✓ |
| 0 | 9.14 | Δ | ✓ |
| 0 | 9.19 | Σ | ✓ |
| 0 | 9.36 | Π | ✓ |
| 0 | 9.55 | Σ | ✓ |
| 0 | 9.88 | Σ | ✓ |
| | | | |
| 1 | 6.88 | Σ | ✓ |
| 1 | 6.98 | Π | ✓ |
| 1 | 7.14 | Δ | x |
| 1 | 7.19 | Σ | ✓ |
| 1 | 7.36 | Π | ✓ |
| 1 | 7.55 | Σ | ✓ |
| 1 | 7.88 | Σ | ✓ |

| v | Series | Symmetry | Observed? |
|---|---|---|---|
| 2 | 6.14 | Δ | x |
| 2 | 6.19 | Σ | ✓ |
| 2 | 6.36 | Π | x |
| 2 | 6.55 | Σ | ✓ |
| | | | |
| 3 | 5.55 | Σ | ✓ |
| 3 | 5.88 | Σ | ✓ |
| | | | |
| 4 | 5.14 | Δ | x |
| 4 | 5.19 | Σ | x |
| 4 | 5.36 | Π | x |
| | | | |
| 5 | 4.88 | Σ | ✓ |

Electronic transition moment **large**

**All v > 1 states that appear in spectrum are $^2\Sigma^+$ states**

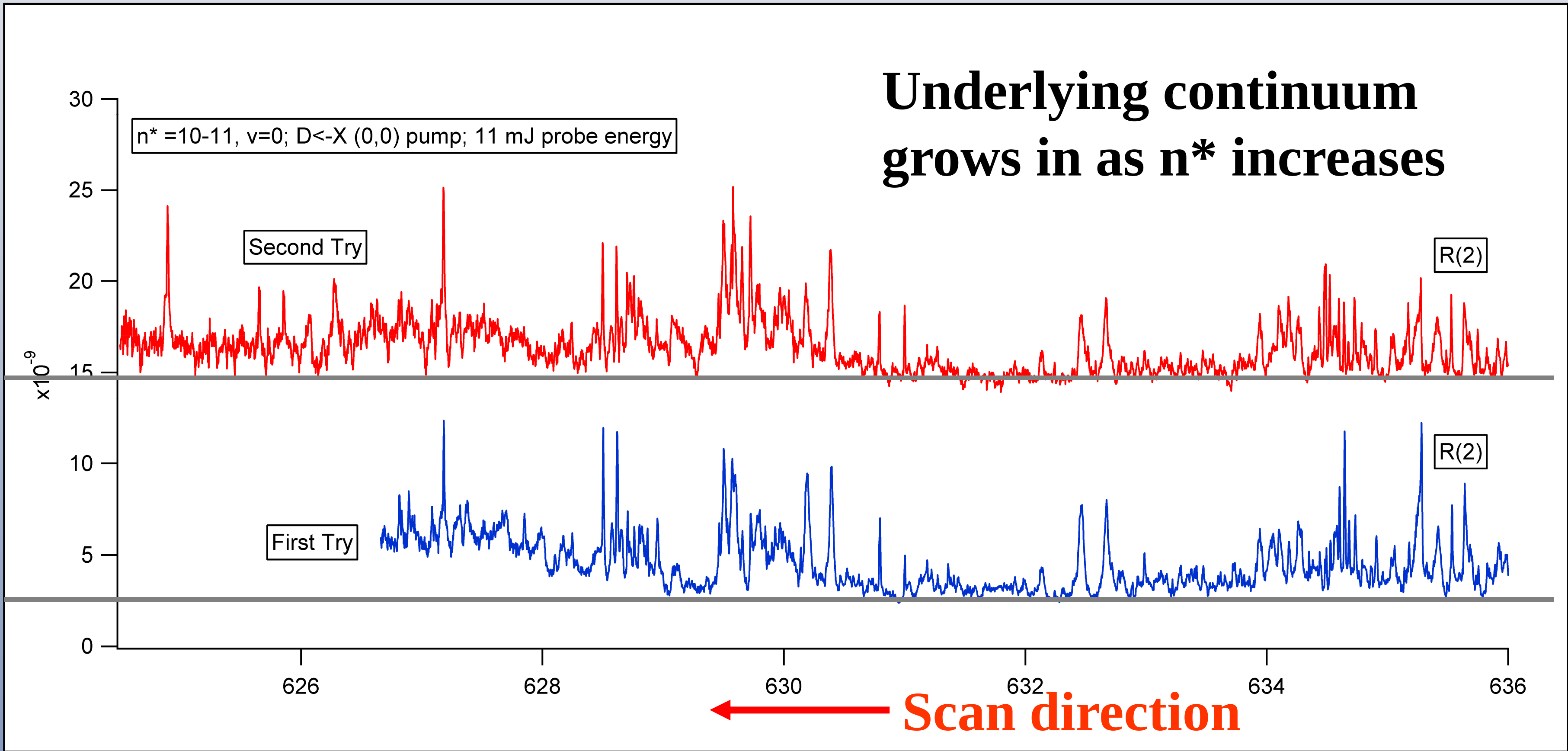
# Fano Lineshapes




**Asymmetric Lineshapes:** interference between transition amplitudes

(But how? Transitions into repulsive state are forbidden.)

# Spectra at Higher Energy:  n*=10-11

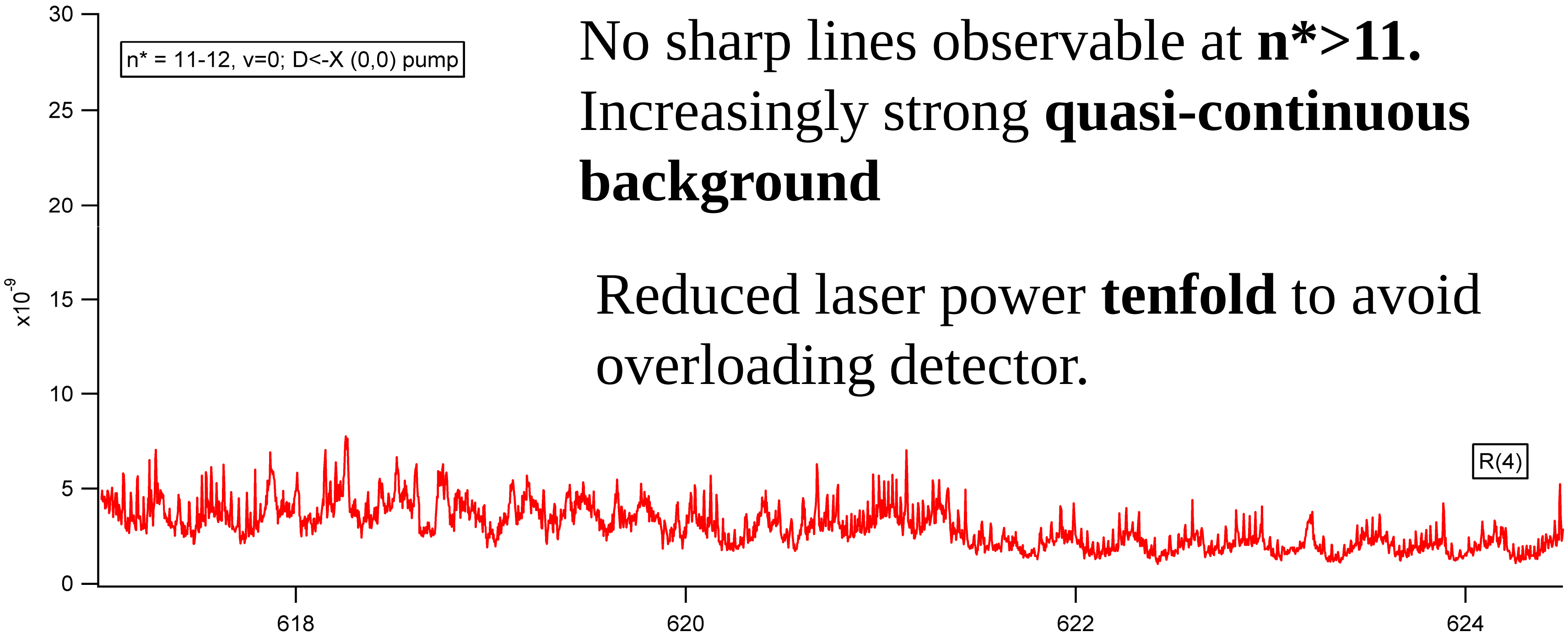



**Underlying continuum grows in as n* increases**

Not a decreasing intensity artifact of Ca rod ablation

Scans performed from **low** to **high** frequency

# Spectra at Higher Energy:  n*=11-12




No sharp lines observable at **n*>11.** Increasingly strong **quasi-continuous background**

Reduced laser power **tenfold** to avoid overloading detector.

Scan direction

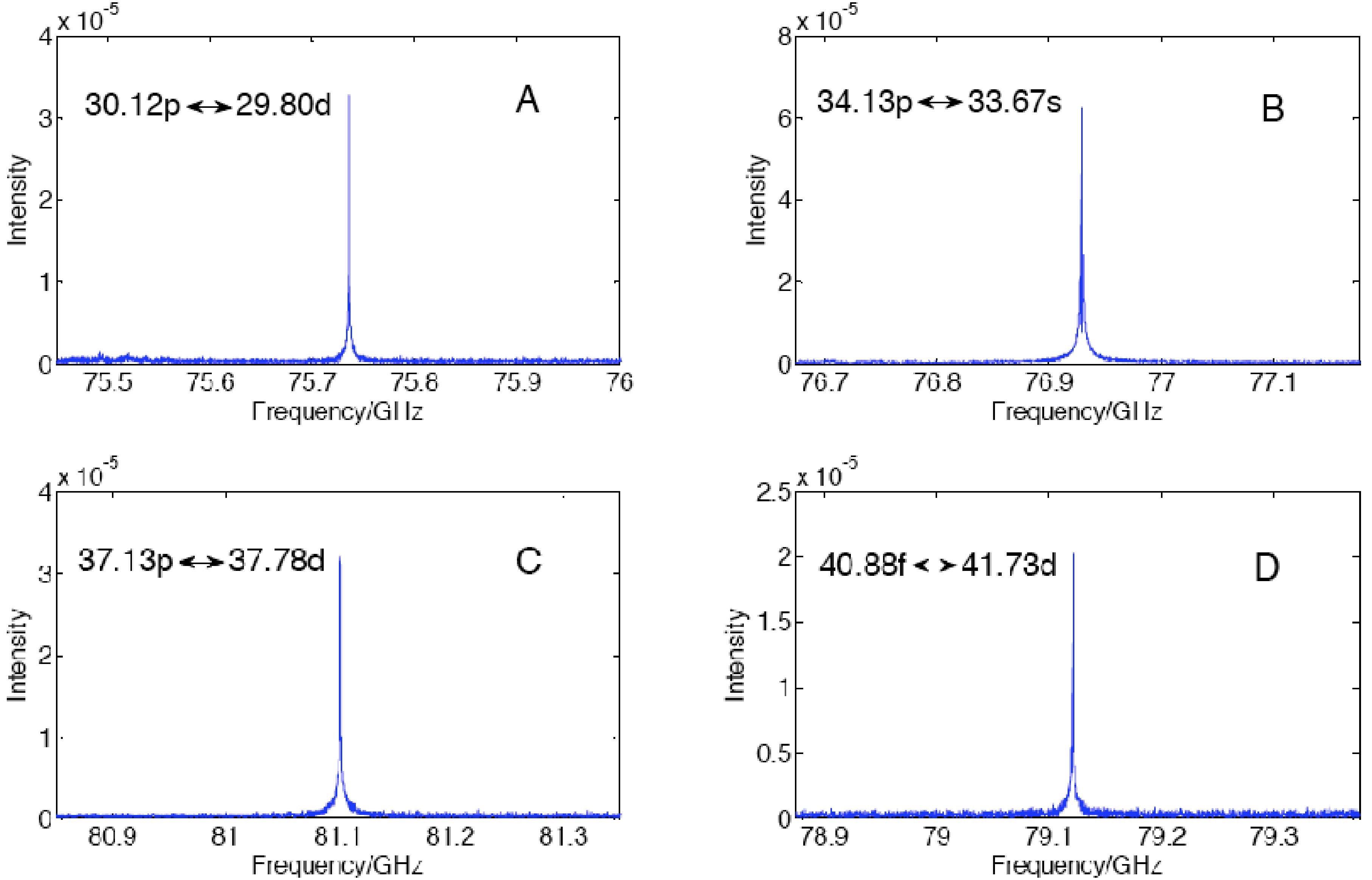
# All Surprising Observations Are Explained by “Indirect” Process

- Mediated by $Ca(4s^2)F(2p\sigma^{-1})$ Vibrational Continuum
- Wrong $\Delta v$ transitions
- Fano Lineshapes
  - $Ca^{2+}F^{-}e^{-}_{Ry} \rightarrow Ca(4s^2)+F(2p\sigma^{-1})$ dissociation continuum transition is forbidden (2 $e^{-}$)
  - $Ca(4s^2)F(2p\sigma^{-1}) \rightarrow Ca^{2+}F^{-} + e^{-}$ ionization continuum transition is forbidden (2 $e^{-}$)
- Quasi-Continuum

# Rydberg-Rydberg Spectra of Ca Atom

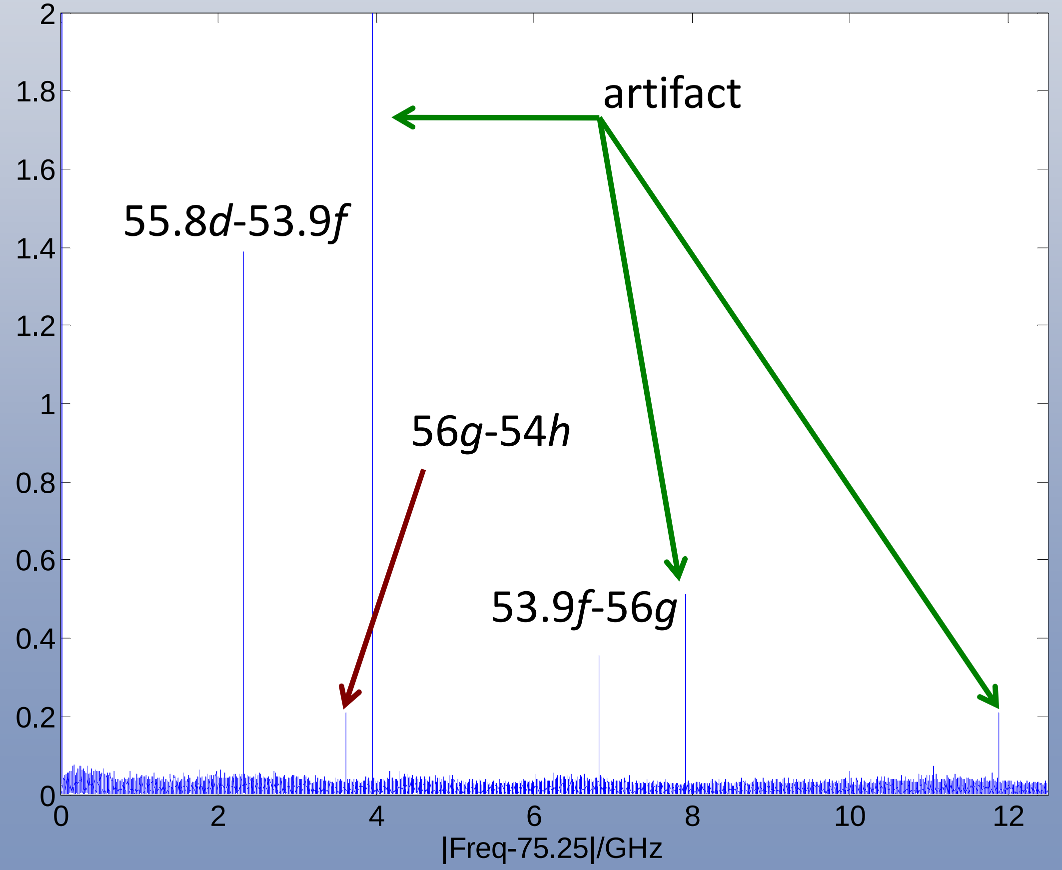
- Optical-Optical-mm Triple Resonance
- FID Detected (FID duration >1 μs)
  - Chirp duration as short as 10 ns
- Crucial apparatus modification: $0.04 \rightarrow 100\ \mathrm{cm}^3$
- 10 GHz search at 1 MHz resolution
- Extend to molecules? Pure electronic spectra?
- Nonpenetrating molecular states
  - $\Delta v^+=0$, $\Delta J^+=0$ ion-core transition selection rules
  - Lifetimes as long as 1 ms
- Must turn off predissociation and autoionization
  - Exploit $n^{-3}$, $\ell^{-10}$ scaling

# FID-Detected Ca Atom Rydberg-Rydberg Electronic Transitions



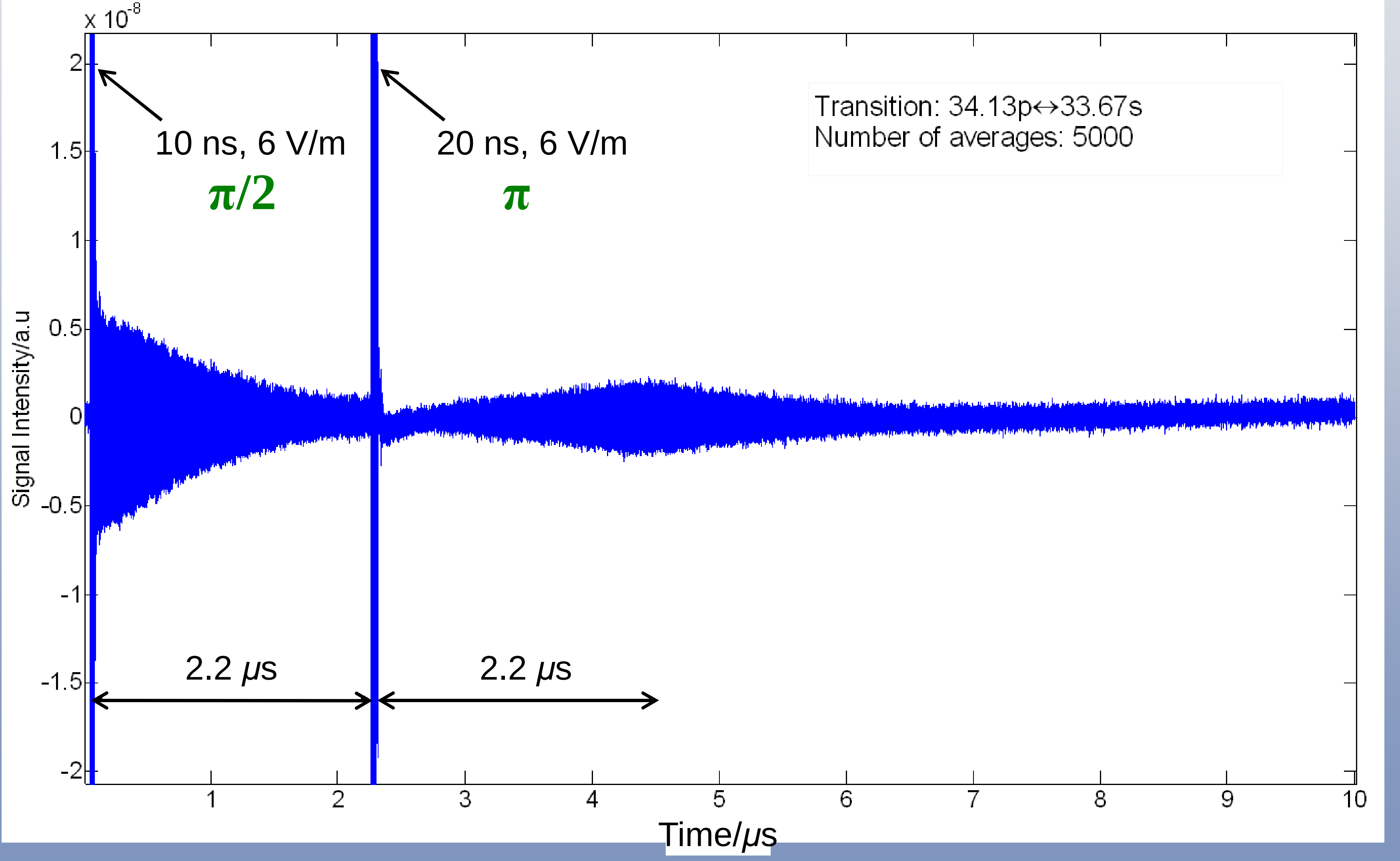
# Climbing a ladder

55.8*d* $\xrightarrow{73\text{GHz}}$ 53.9*f* $\xrightarrow{82\text{GHz}}$ 56*g* $\xrightarrow{79\text{GHz}}$ 54*h* $\xrightarrow{80\text{GHz}}$ 56*i* .......

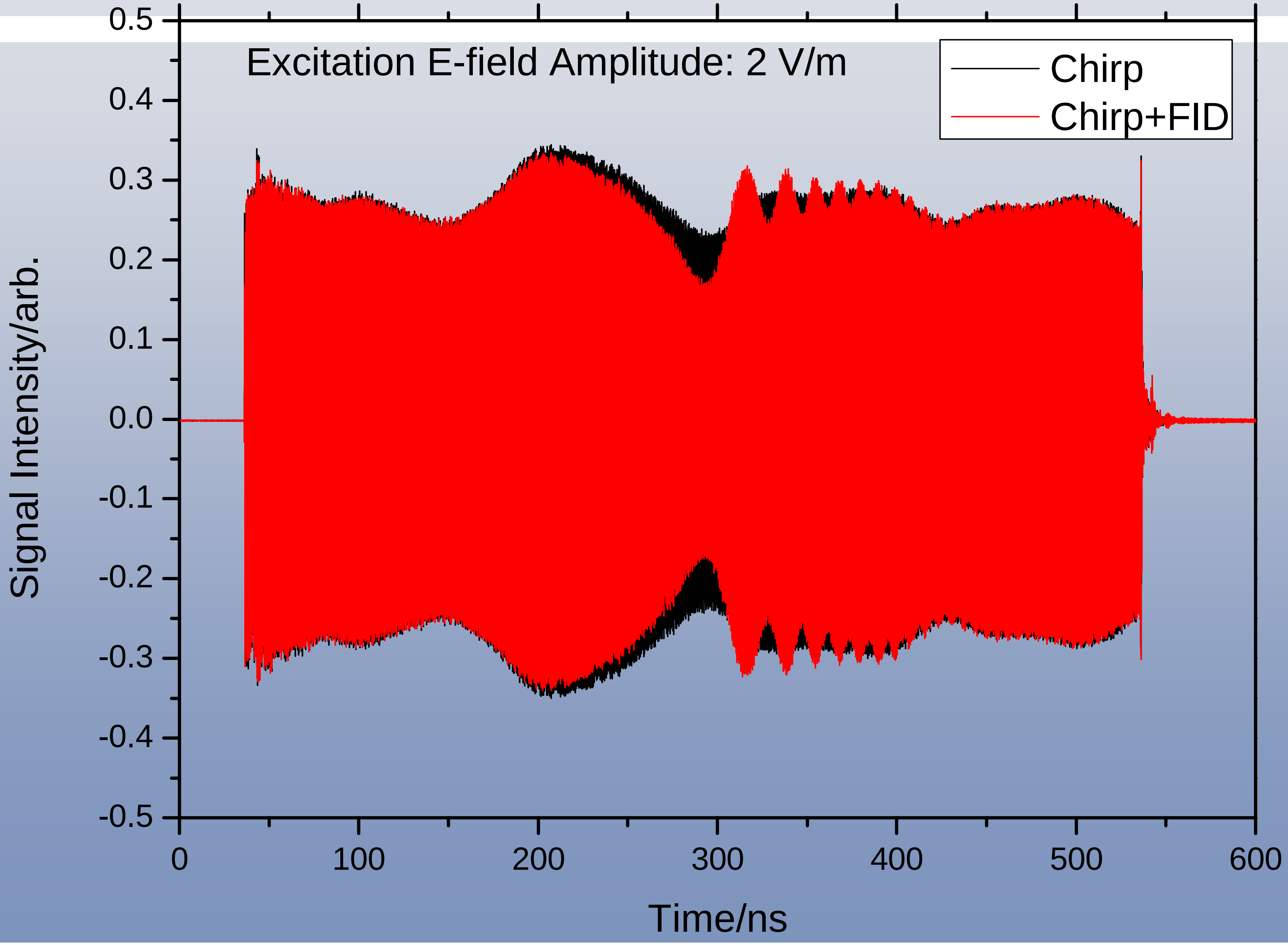



5,000 averages

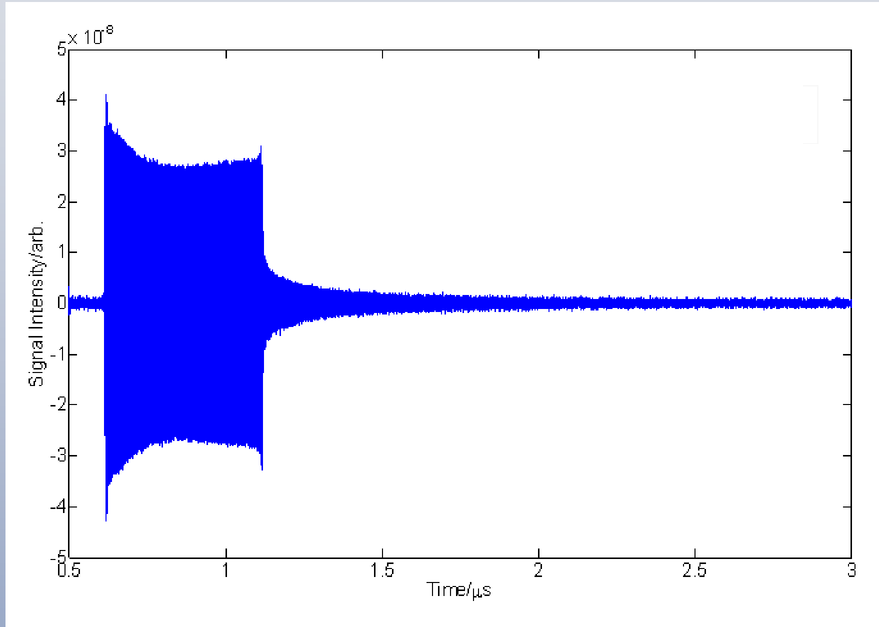
# Millimeter-Wave Photon Echo



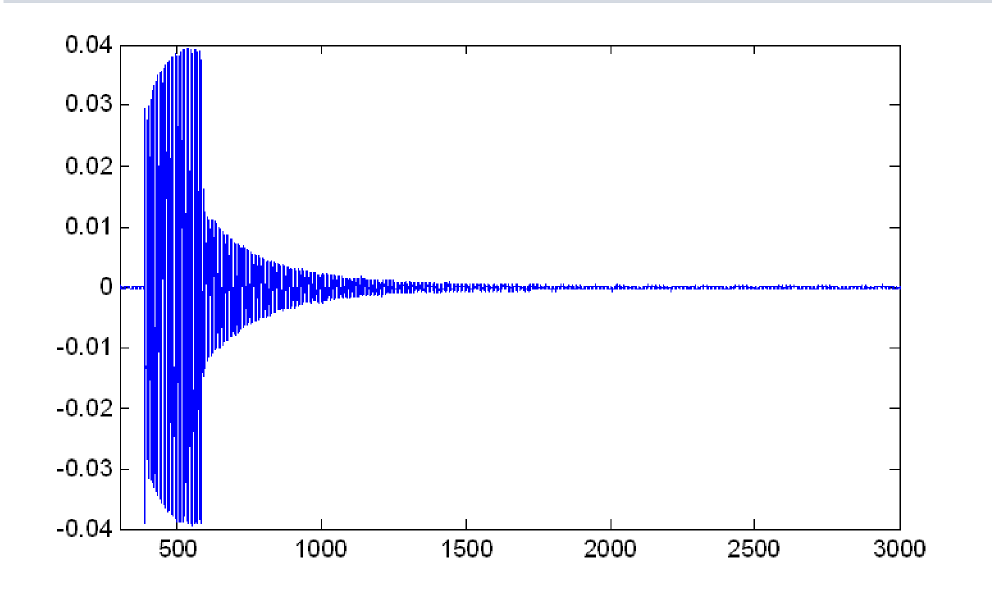
# FID During a Chirp



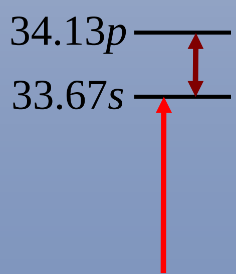
# Which way is up?

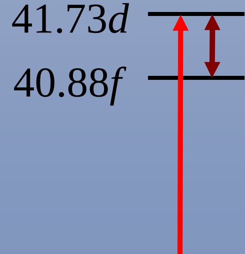



Time/μs




Time/ns

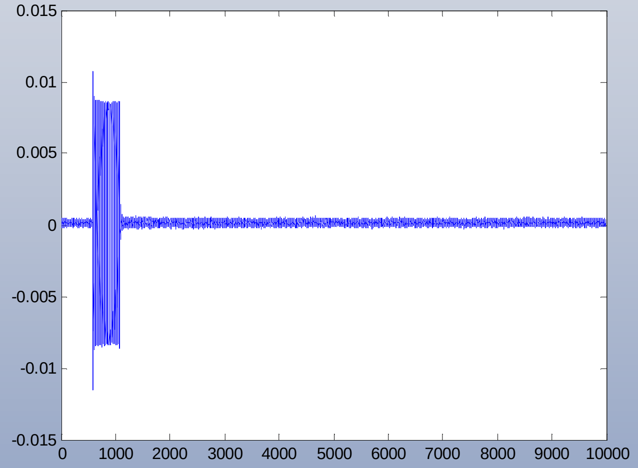


# Calcium Atoms

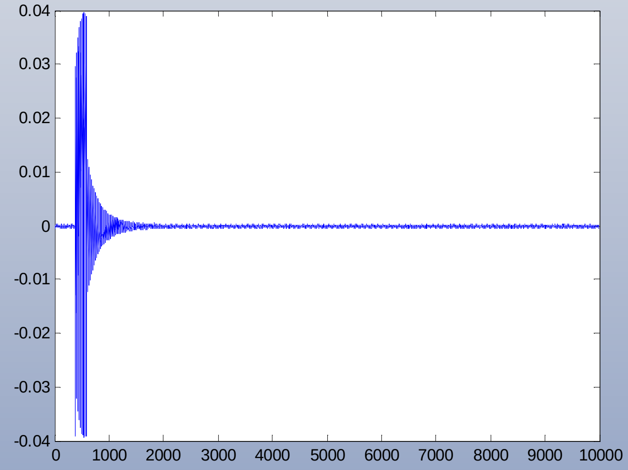
## Fitted Phase Difference: FID-mmW Pulse

$34.13p - 33.67s$




1.08(2) π

$41.73f - 40.88d$



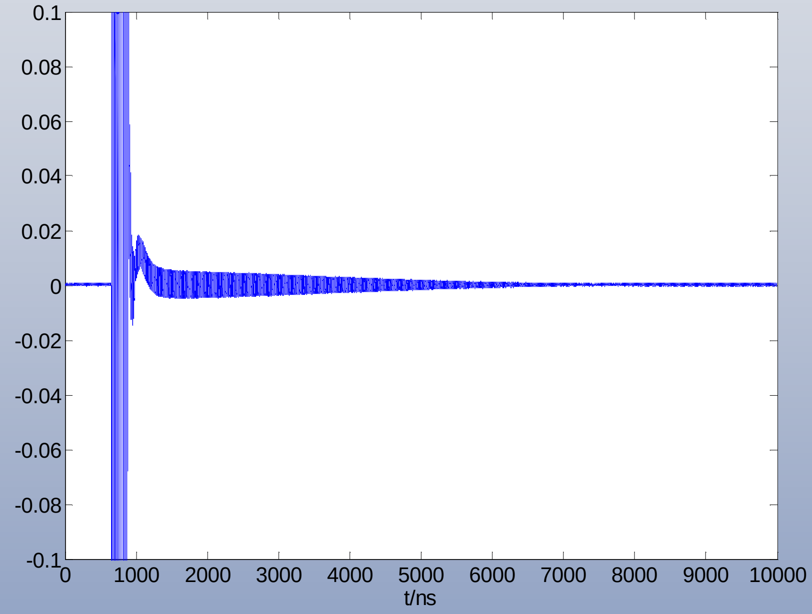

0.04(1) π

Single frequency excitations

Uncertainties in () are the 95% confidence intervals

# $SO_2$: $\pi$/100 Polarizing Pulse
## Chirp-FID Phase Difference

$6_{06}$ - $5_{15}$



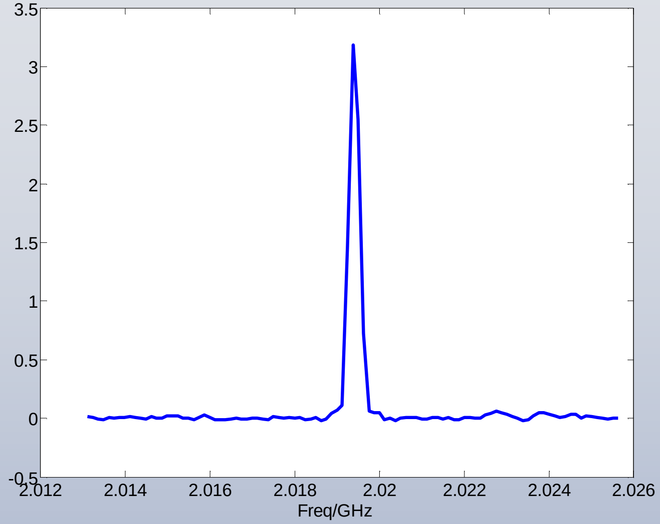

1.01(2) π

Oscilloscope truncated-Chirp, fitted to only ~1% of the chirp amplitude
chirp duration 500 ns
chirp bandwidth 5 GHz

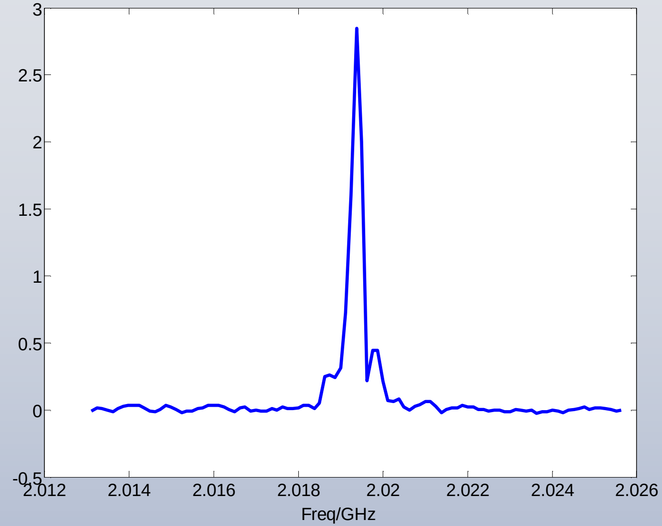
Uncertainty in () is 95% confidence interval

# “Optical” Nutation: A Small Step from Superradiance

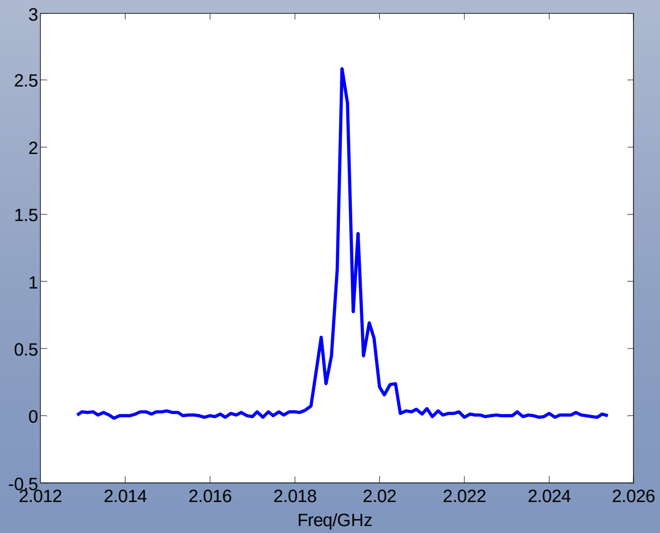
N<1 × $10^5$/$cm^3$, ~π/2 ex_pulse



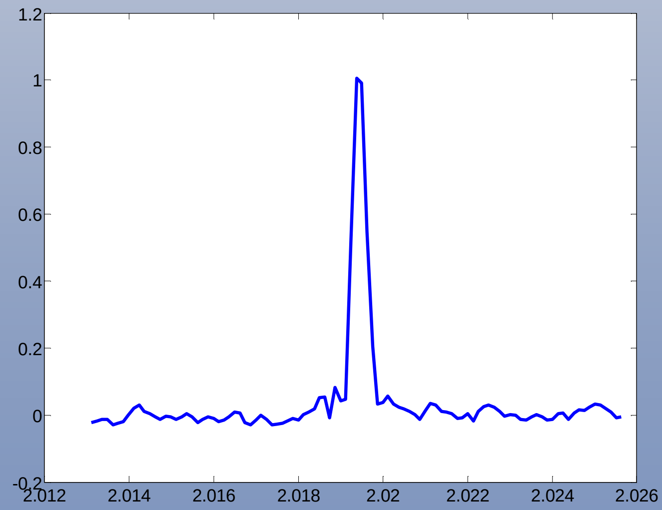

N~1 × $10^5$/$cm^3$, ~π/2 ex_pulse



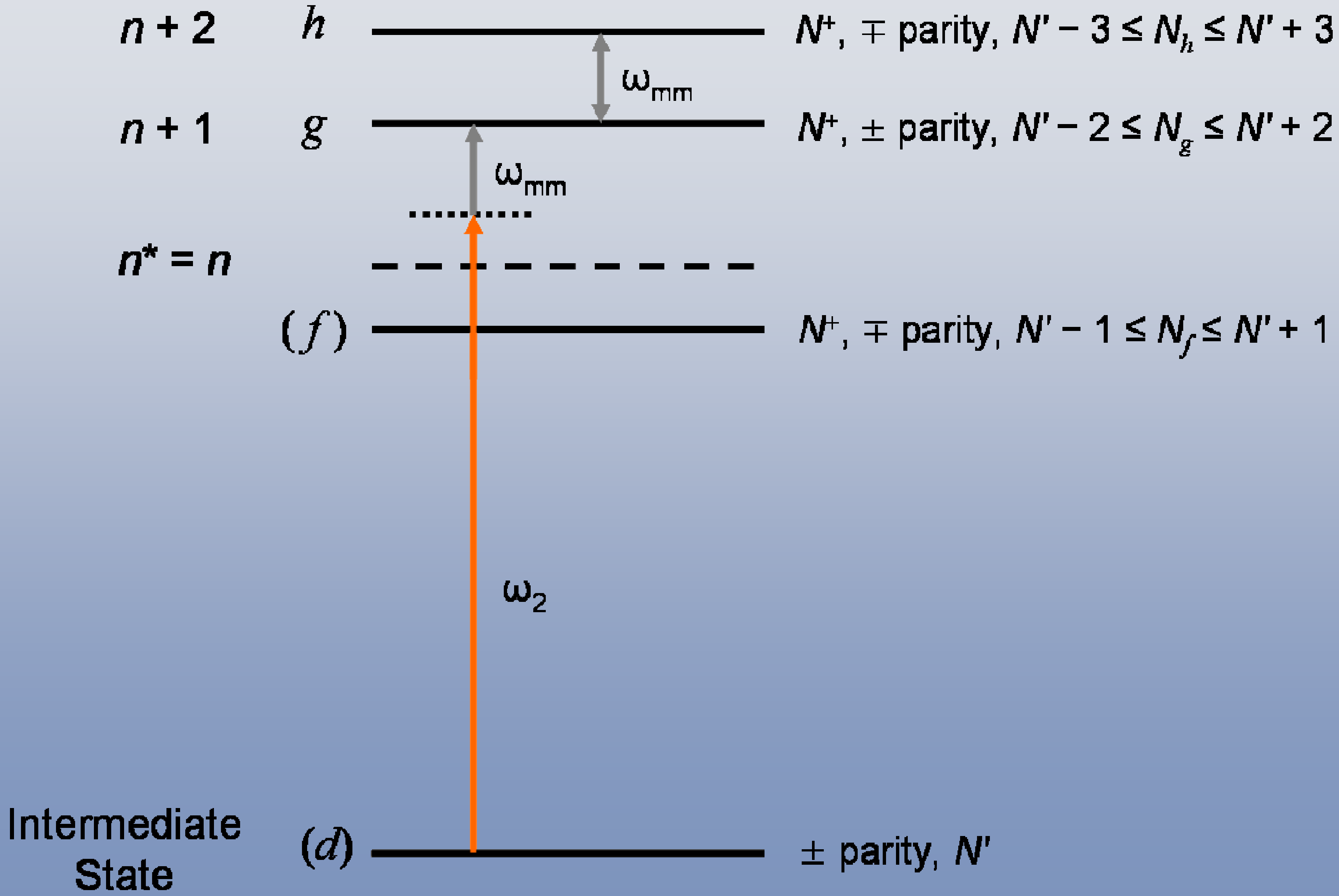

N~3 × $10^5$/$cm^3$, ~π /2 ex_pulse



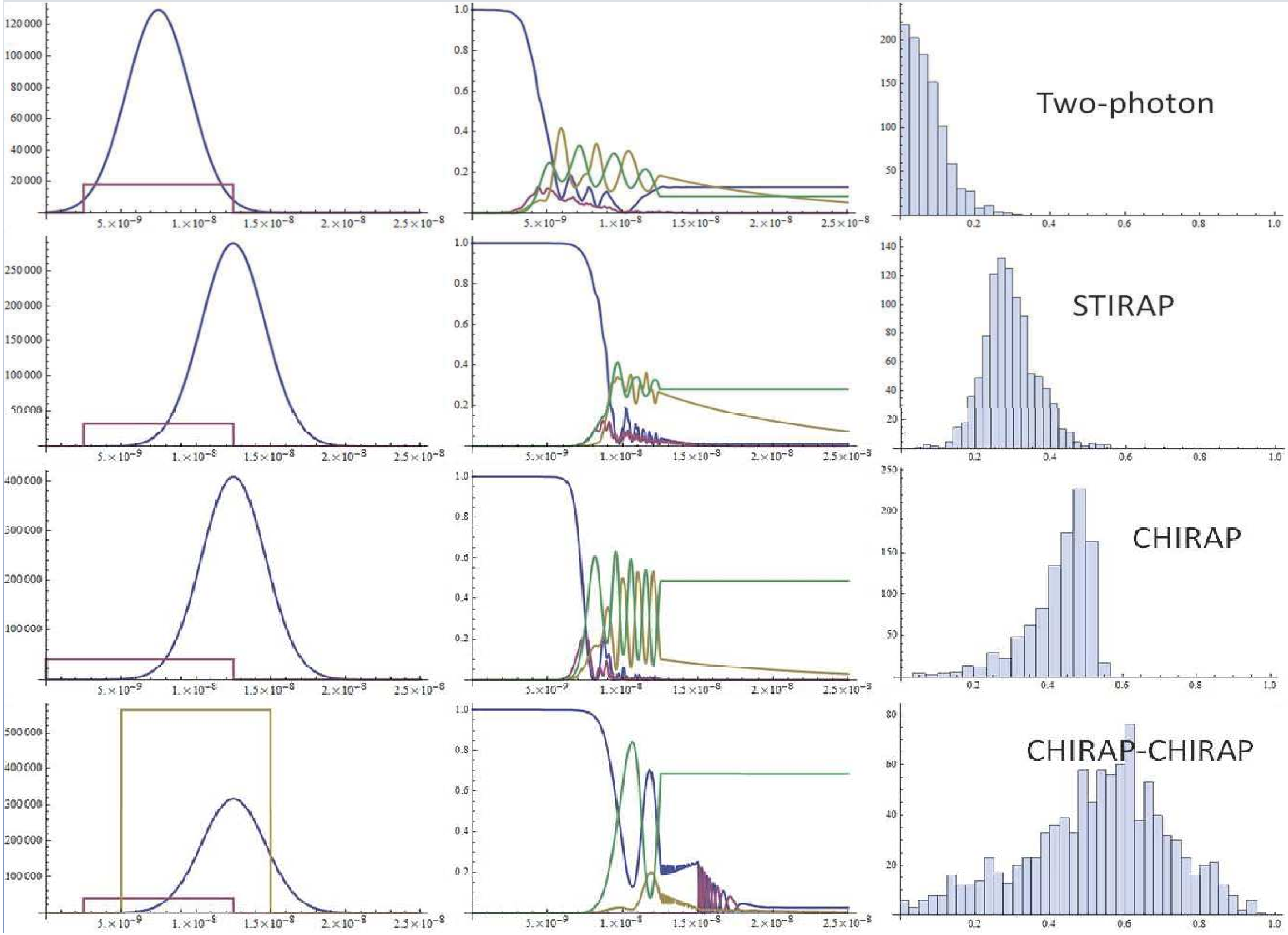

N~3 × $10^5$/$cm^3$, ~π ex_pulse



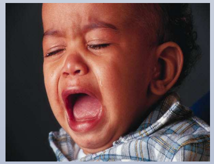
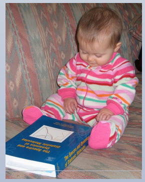
# How to Jump Over the Zone of Death



# Jumping Over the Zone of Death



# Conclusions

- CaF: complete experimental determination of quantum defect matrix
  - All spectra, all dynamics!
- Tedious detective work:  or  ?
- Need higher resolution, meaningful intensities, and escape from fast nonradiative decay
- FID-detected Rydberg-Rydberg spectra!
  - $>10^3$ Debye transition moment at $n^* \approx 20$
  - pure electronic Rydberg-Rydberg spectra

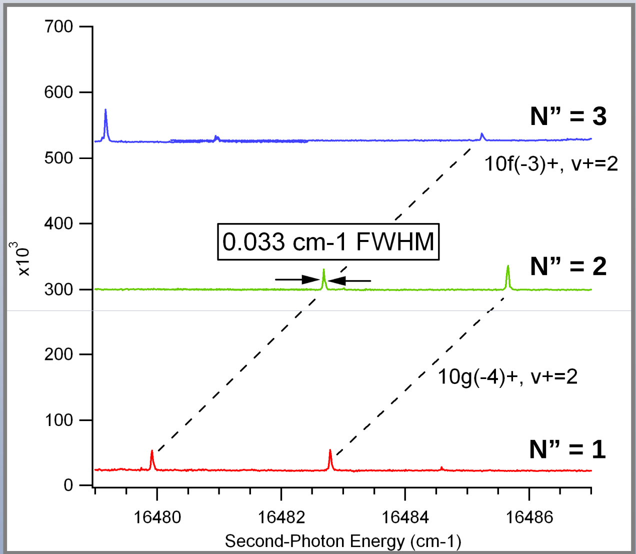
# Who Did This?

- Peter Bernath
- Mike Dulick LFT
- Bernard Pinchemel (Lille)
- Richard Barrow (Oxford) LFT
- Precila Ip BaF
- Steve Rice LFT
- David Baldwin CaO
- Jim Murphy MQDT
- Jon Berg
- Anthony Merer (UBC)
- Nicole Harris
- Chris Gittins
- Zygmunt Jakubek BaF
- Foss Friedman-Hill
- Leonid Kaledin
- Ed Murad (AFGL)
- Mike McCarthy
- Jon Bloch
- Jian Li (Tsinghua)
- Yaoming Liu (Tsinghua)
- Dave Moss
- Jason Clevenger CaCl
- Ma Hui (Tsinghua)
- Xing Jiang
- Dan Byun
- **Jeff Kay** Spectra + MDQT Fit*****
- Vladimir Petrovic
- **Christian Jungen** MQDT (Orsay)
- **Serhan Altunata** MQDT
- Steve Coy MQDT
- Bryan Wong MQDT
- **Kirill Kuyanov** CPmmW*****
- **Yan Zhou** CPmmW*****
- **Tony Colombo** CPmmW*****
- **Barratt Park** CPmmW*****
- $$$ NSF

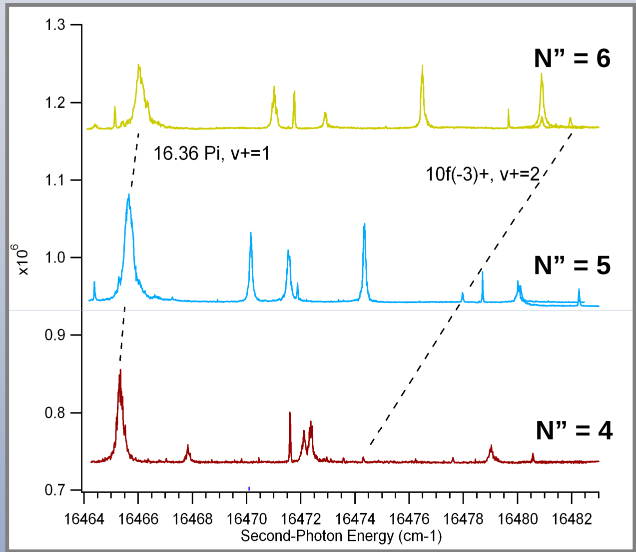
# CaF Rydberg Papers

- spdf QD **μ** Matrix: Gittins, JCP **122** 184314 (2005)
- Ab Initio **R**-Matrix: Wong, JCP 124 014106 (2006)
- Shape Resonance, Altunata, JCP **124** 194302 (2006)
- Resonances: Kay, Mol. Phys. **105** 1661 (2007)
- fgh...∞ Nonpenetrating: Kay, JCP **128** 194301 (2008)
- Polarization: Petrović, JCP **128** 014301 (2008)
- Stark Effect: Petrović, JCP 131 064301 (2009)
- spdf QD **μ**(R,E) Matrices: Kay, final preparation

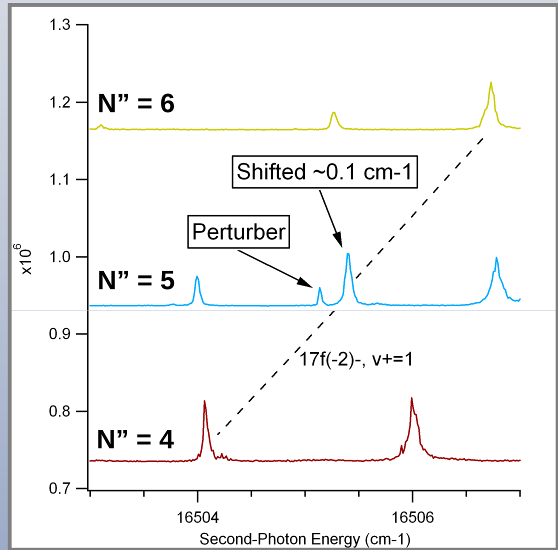
# Improved Quality of Jeff Kay's Spectra: Resolution, Precision, Dynamic Range, Continuous Range of *n** and *N*




Resolution
widths, splittings




Dynamic Range
weak lines




Precision
tiny level-shifts

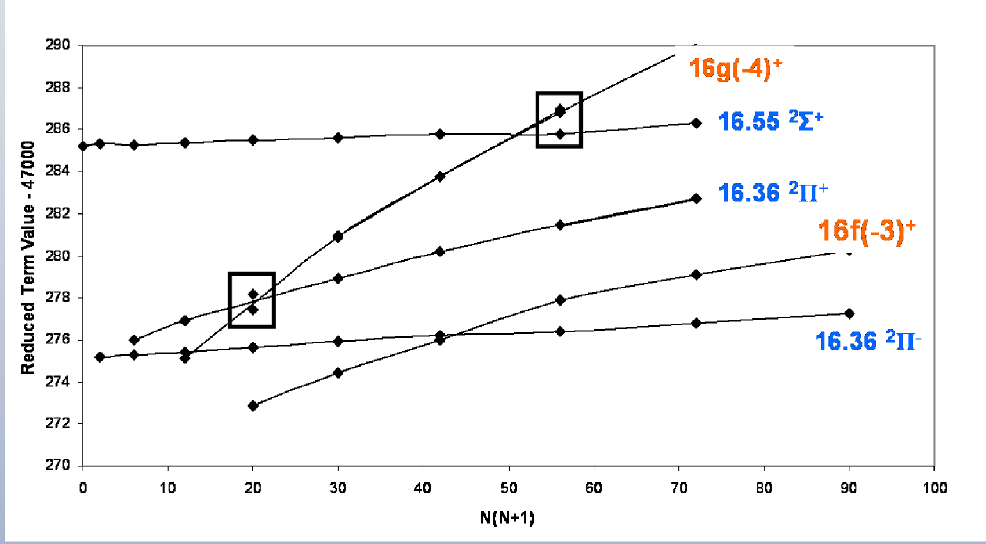
Data set specifics: resolution: 0.03 $cm^{-1}$
calibration error: <0.01 $cm^{-1}$ rms
rotational levels: $0 < N < 9$
energy range: $5<n^*<10$ ($v^+=0$), $16<n^*<21$ ($v^+=1$)

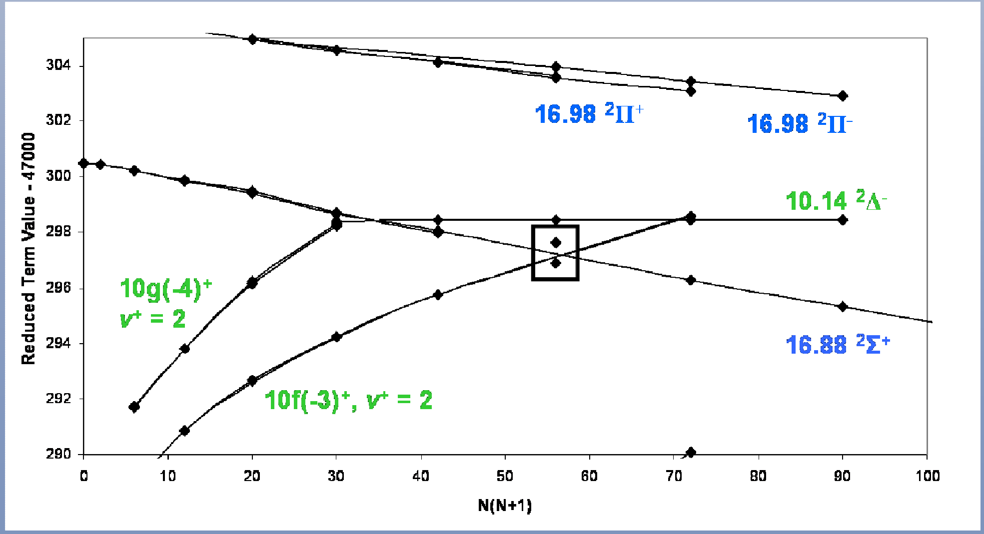
# A Zoology of Perturbations: Δv =0 ℓ-Mixing and ℓ -Uncoupling; Δv ≠ 0 due to μ(*R*) and B(*R*)

- Perturbations between penetrating and nonpenetrating states:
  - 16g(-4)$^+$ ~ 16.36 $^2\Pi^+$
  - 16g(-4)$^+$ ~ 16.55 $^2\Sigma^+$
  - 17g(-4)$^+$ ~ 17.36 $^2\Pi^+$
  - 17g(-4)$^+$ ~ 17.55 $^2\Sigma^+$
  - 10f(-3)$^+$ $v^+ = 2$ ~ 16.88 $^2\Sigma^+$

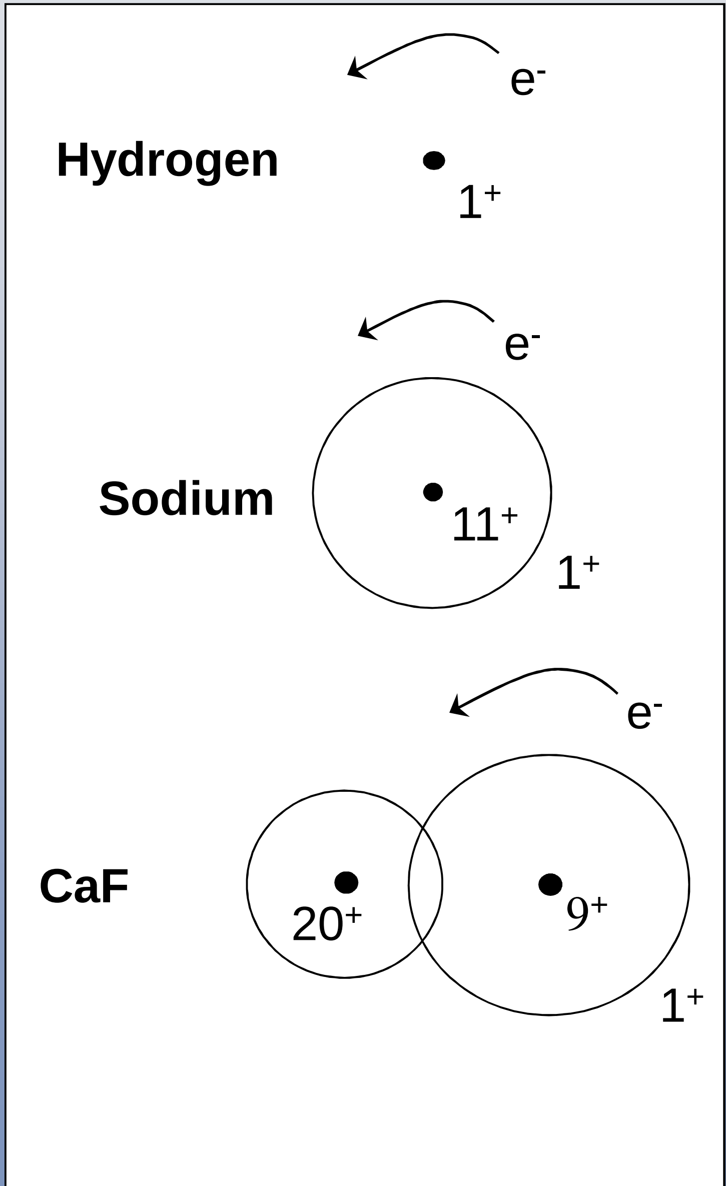
- Matrix elements range from <0.1 cm$^{-1}$ to >1 cm$^{-1}$

- Perturbations sample core dipole, higher multipole moments, polarizability, and the *R*,*E*-derivatives of quantum defect matrix elements.



# Multichannel Quantum Defect Theory (1)




$$\boxed{E_{n\ell} = -\frac{\Re}{n^2}}$$

$$n = \ell + 1, \ell + 2, \ldots \infty$$

independent of $\ell$

$$\boxed{E_{n\ell} = -\frac{\Re}{\underbrace{(n-\delta_\ell)}_{n^*}{}^2}}$$

$\pi\delta_\ell$ is phase shift (relative to H)

$$n^*,\ \ n^*+1,\ \ n^*+2,\ \ \ldots\ \ \infty$$

$\delta_\ell$ is quantum defect

- independent of $n$
- dependent on $\ell$

$$V_\ell(r) = -\frac{Z^{eff}(r)}{r} + \frac{\ell(\ell+1)}{2m_e r^2}$$

$$\boxed{E_{n\ell\lambda} = -\frac{\Re}{\left(n-\mu_\alpha(R)\right)^2}}$$

Eigenquantum defect $\mu_\alpha(R)$

- R-dependent
- mixed $\ell$

$$0 = \left|\mathbf{K} + \mathbf{P}(E)\right|$$

$$\Big\downarrow\ \mathbf{K} = \tan \pi\boldsymbol{\mu}$$

$$\boldsymbol{\mu}(R,E) = \boldsymbol{\mu}(R_e^+) + \frac{d\boldsymbol{\mu}}{dR}(R - R_e^+) + \frac{d\boldsymbol{\mu}}{dE}E$$

$\mathbf{K}(R,E)$ reaction matrix

$\mathbf{P}(E)$ phase matrix

$\boldsymbol{\mu}(R,E)$ quantum defect matrix

$\mathbf{H}^{eff}$ vs. $\mathbf{K},\mathbf{P}$

# Multichannel Quantum Defect Theory (2)

Eigenvalue Condition: $$0 = \left| \underbrace{\mathbf{K}^{(N,p)}}_{\text{Reaction Matrix}} + \underbrace{\mathbf{P}(E)^{(N,p)}}_{\text{Phase Matrix}} \right|$$

*N* (rotation), $\Lambda$, and *p* (parity) are Good Quantum Numbers

Elements of **Non-Diagonal** Reaction Matrix:

$$K_{\ell,\ell'}^{(\Lambda)}(R) = \tan \pi \mu_{\ell,\ell'}^{(\Lambda)}(R)$$

Elements of **Diagonal** Phase Matrix:

$$P_{\ell \mathrm{v}^+ N^+, \ell \mathrm{v}^+ N^+}(E) = \tan \pi \nu_{\mathrm{v}^+ N^+}(E)$$

Effective Principal Quantum Number

$$n^* = \left[ \frac{\Re}{E_{\mathrm{v}^+ N^+} - E} \right]^{1/2} = \nu_{\mathrm{v}^+ N^+}(E)$$

# Frame Transformations

## fancy name for free stuff from $\mu^{(\Lambda,p)}(R)$

- Ion-core vibrational wavefunctions: $\chi_{v+}(R)$

$$\int dR \chi_{v+}(R)\mu^{(\Lambda,p)}_{\alpha\alpha'}(R)\chi_{v+'}(R) = \mu^{(\Lambda,p)}_{\alpha v+,\alpha' v+'}$$

  – Inter-series $\Delta v^+ \neq 0$ perturbations

  – Vibrational autoionization

- Long-range coupling of Rydberg $e^-$ angular momentum to angular momentum of molecular frame: $\dot{\mathbf{N}} = \dot{\mathbf{N}}^+ + \dot{\mathsf{l}}$
  - $\ell_R = N^+ - N$
  - $N^+$ is pattern-forming [$B^+N^+(N^+ +1)$], $N$ is conserved
  - Case (b) to (d) transformation of $\mu^{(\Lambda,p)}$: 3-j coefficients

$$< l N^+ N | l \Lambda N >< l \Lambda N | \mu^{(\Lambda,p)} | l' \Lambda N >< l' \Lambda N | l' N^{+\prime} N >$$

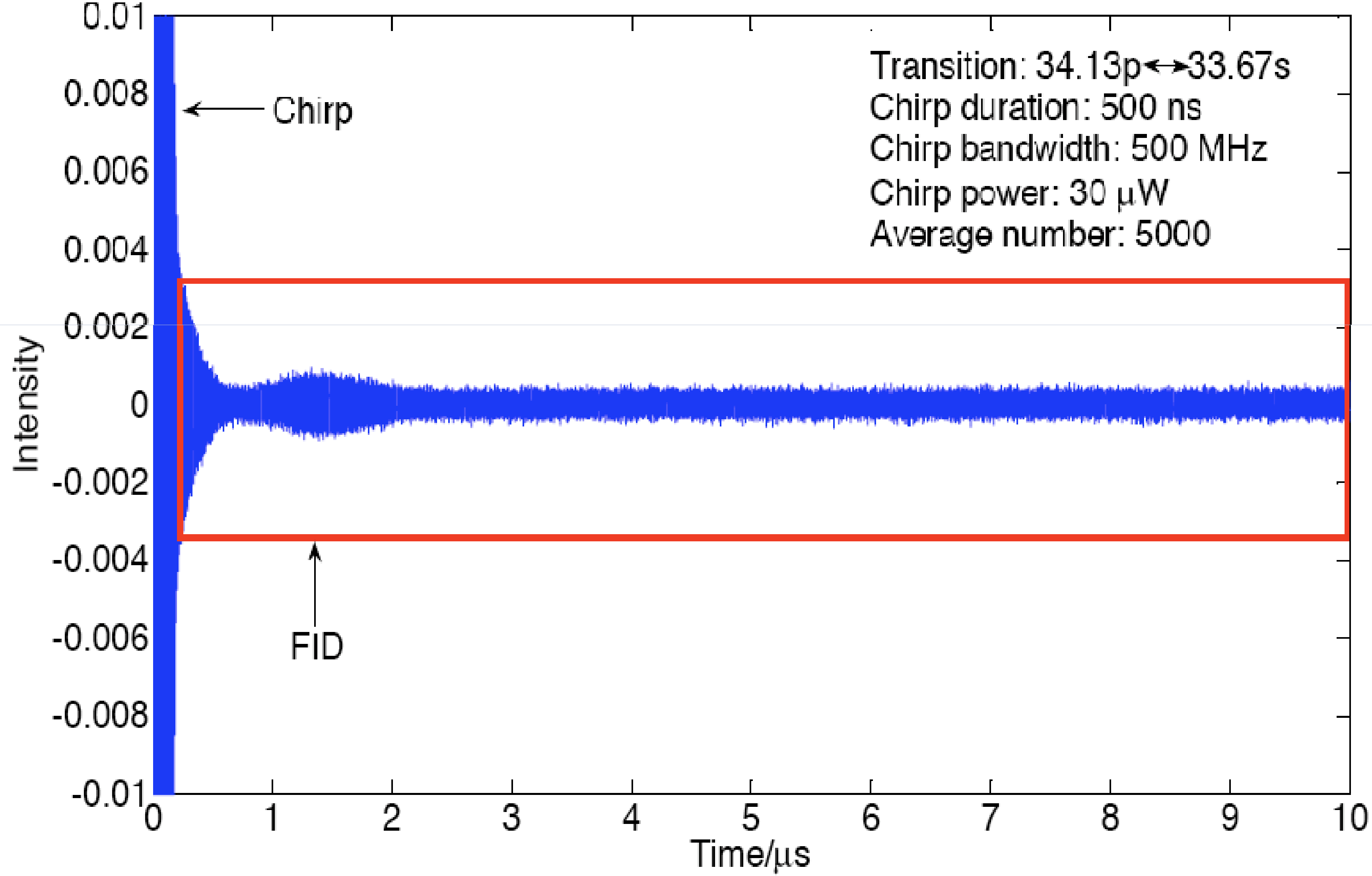
| | $\mu(R_e^+,\varepsilon=0)$ | $\partial\mu/\partial R$ | $\partial\mu/\partial E$ | $\partial^2\mu/\partial R^2$ | $\partial^2\mu/\partial E^2$ | $\partial^2\mu/\partial E\partial R$ |
|---|---|---|---|---|---|---|
| ss Σ | 0.3503(8) | -0.0720(73) | 1.884(0) | 1.147(25) | -54.27(24) | -4.31(30) |
| pp Σ | 0.2224(10) | 0.3860(11) | -0.793(70) | -1.132(33) | 54.75(198) | -5.60(11) |
| dd Σ | -0.1350(2) | 0.1095(45) | -0.084(30) | 0.734(3) | 33.56(15) | |
| ff Σ | -0.1100(8) | 0.0930(105) | | 0.508(36) | -29.36(223) | 7.12(43) |
| sp Σ | 0.1553(1) | 0.0217(17) | -0.198(23) | -0.579(10) | | |
| pd Σ | 0.04048(14) | | -0.977(71) | 0.178(44) | | |
| df Σ | -0.0583(7) | | 0.117(62) | 0.202(9) | 6.15(245) | 3.72(10) |
| sd Σ | -0.0369(19) | -0.1085(19) | -3.239(0) | | | |
| pf Σ | | 0.1121(59) | -0.138(114) | | | |
| sf Σ | -0.0466(31) | -0.0796(38) | | | | |
| pp Π | -0.1758(6) | 0.3348(16) | 3.404(15) | -0.629(11) | 6.11(79) | |
| dd Π | -0.1429(4) | 0.3559(26) | -2.975(14) | 0.503(13) | -4.16(43) | 11.12(0) |
| ff Π | -0.0400(4) | 0.0539(57) | -0.347(21) | | | |
| pd Π | 0.1718(2) | -0.1395(16) | 0.091(17) | 0.425(9) | -62.89(68) | |
| df Π | -0.0148(6) | | | | 7.69(11) | |
| pf Π | 0.0402(7) | 0.0320(24) | -0.974(33) | | | |
| dd Δ | -0.1336(3) | 0.2606(9) | -0.047(4) | | | |
| ff Δ | 0.0235(3) | 0.0891(19) | | | | |
| df Δ | -0.0317(6) | -0.0339(12) | | | | |
| ff Φ | 0.0959(1) | 0.2280(19) | | | | |

**The complete quantum defect matrix, μ(E,R), for the s,p,d,f core-penetrating states. All spectra, all dynamics…**

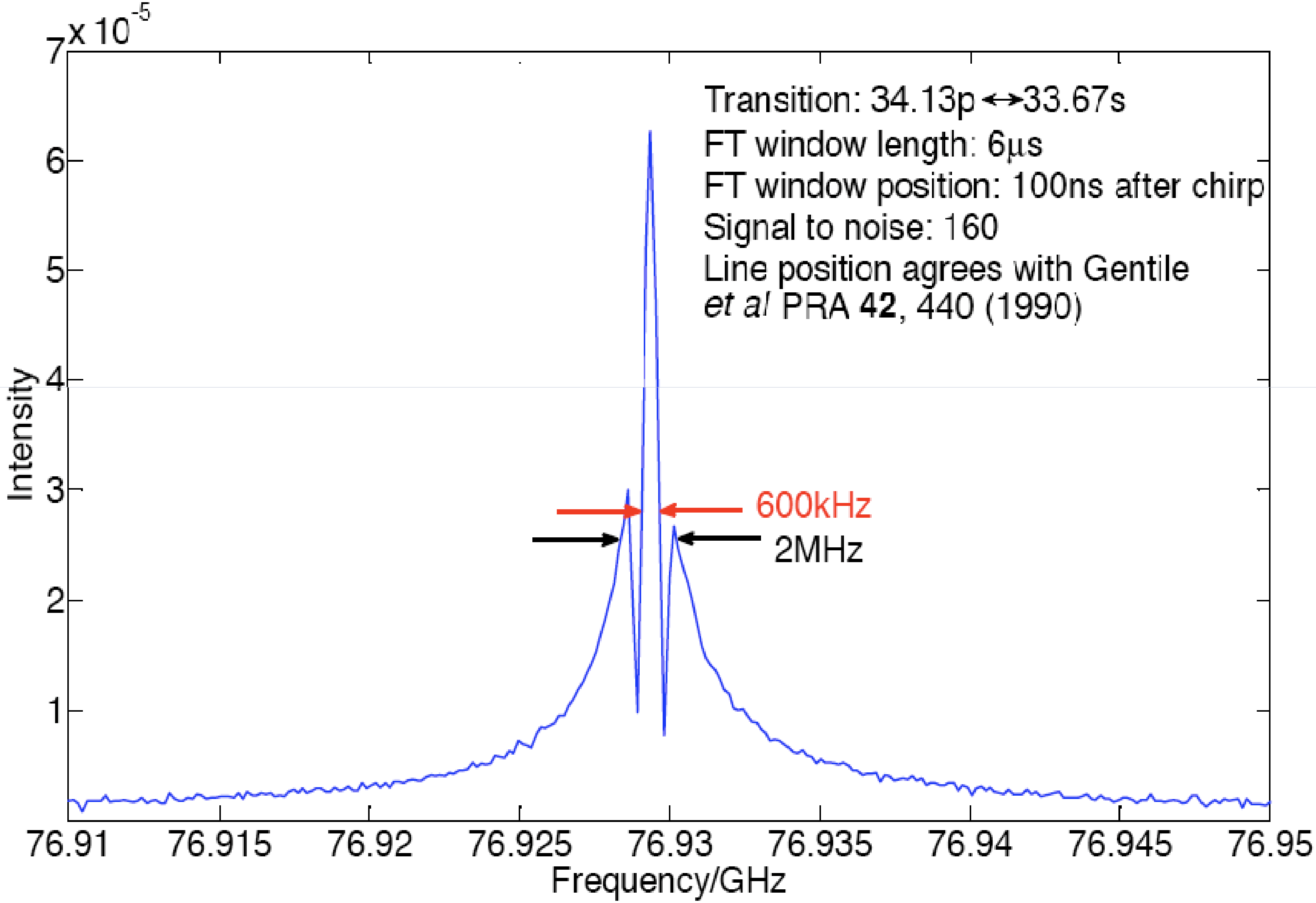
# What Do These Matrix Elements Tell Us?

- Consequences of Not-Roundness
  - R-dependence
- Perturbations and Autoionization
  - Rates of dynamical processes
  - Where to look for specific class of process
- Unmet Challenge: Simple Reasons for Observed Values?
  - Relationships among $\mu$, $d\mu/dR$, $d\mu/E$ elements?
    - Find a more compact and physical representation?
  - Unusual E dependence of one $\mu_\alpha$
    - a shape resonance

# Chirp and FID



# CPmmW Lineshape: 5000 Shots



# Semi-Classical Resonances

**Any two intramolecular motions may be tuned to have the same period**

Kepler Period $$T_{Kepler}(n^*) = \frac{h}{E_{n^*+1/2} - E_{n^*-1/2}} = \frac{h}{2hc\Re/n^{*3}} \propto n^{*+3}$$

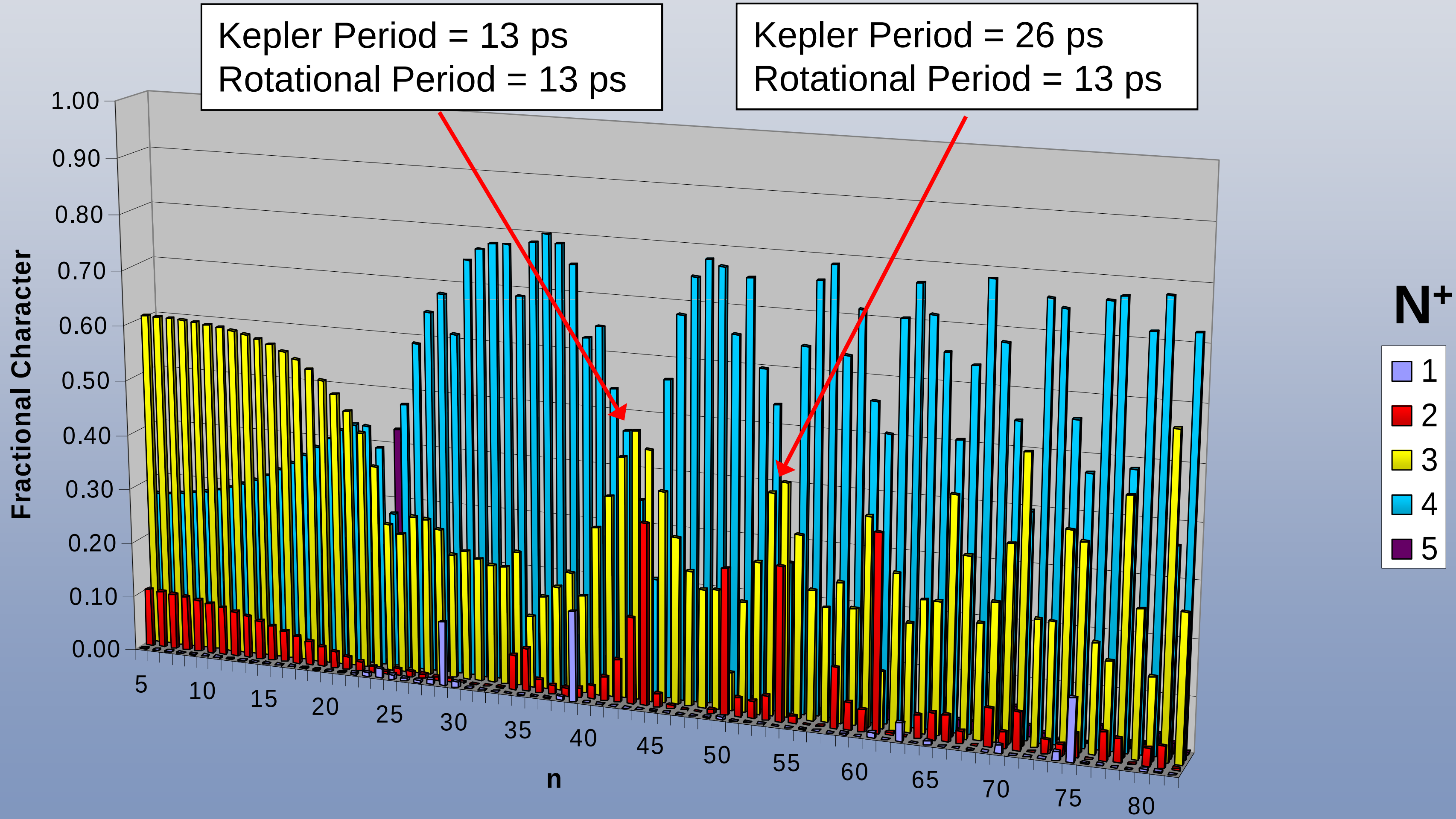
Vibrational Period $$T_{vib}(\mathrm{v}) = \frac{h}{(E_{\mathrm{v}+1} - E_{\mathrm{v}-1})/2} = \frac{h}{hc\omega_e} \propto \mathrm{v}^0$$

Rotational Period $$T_{rot}(N) = \frac{h}{(E_{N+1} - E_{N-1})/2} = \frac{h}{hcB[2N+1]} \propto N^{-1}$$

Multipole Precession $$T_{\mu,Q}(\lambda) = \frac{h}{(E_{\lambda+1} - E_{\lambda-1})/2} \propto \frac{1}{(\mu^2 - Q)\lambda} \propto \lambda^{-1}$$

At a selected ***resonance***, energy flows rapidly between two *selected* modes. Away from resonance, the two modes are *dynamically decoupled*.

# Stroboscopic Effects




**'p' Π Series; *N* = 3**

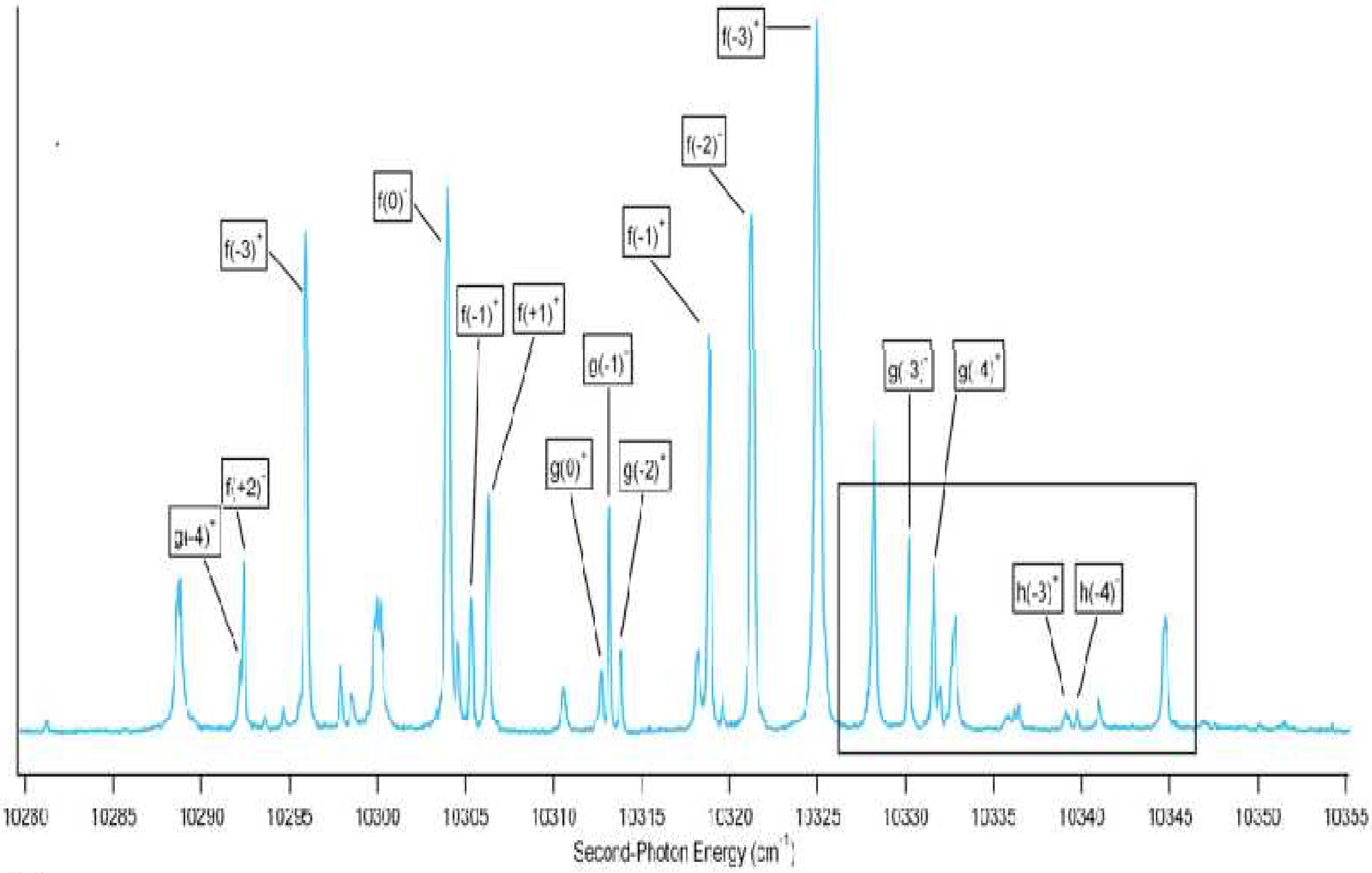
# Long Range Model

- Ion-Core Electronic Structure
  - **μ**, **Q**, **O**, **H** moments
  - α, γ dipole polarizability components
- Fancy Computer-Automated Algebra
  - Observed splittings near integer n* (need very high resolution)

⬇

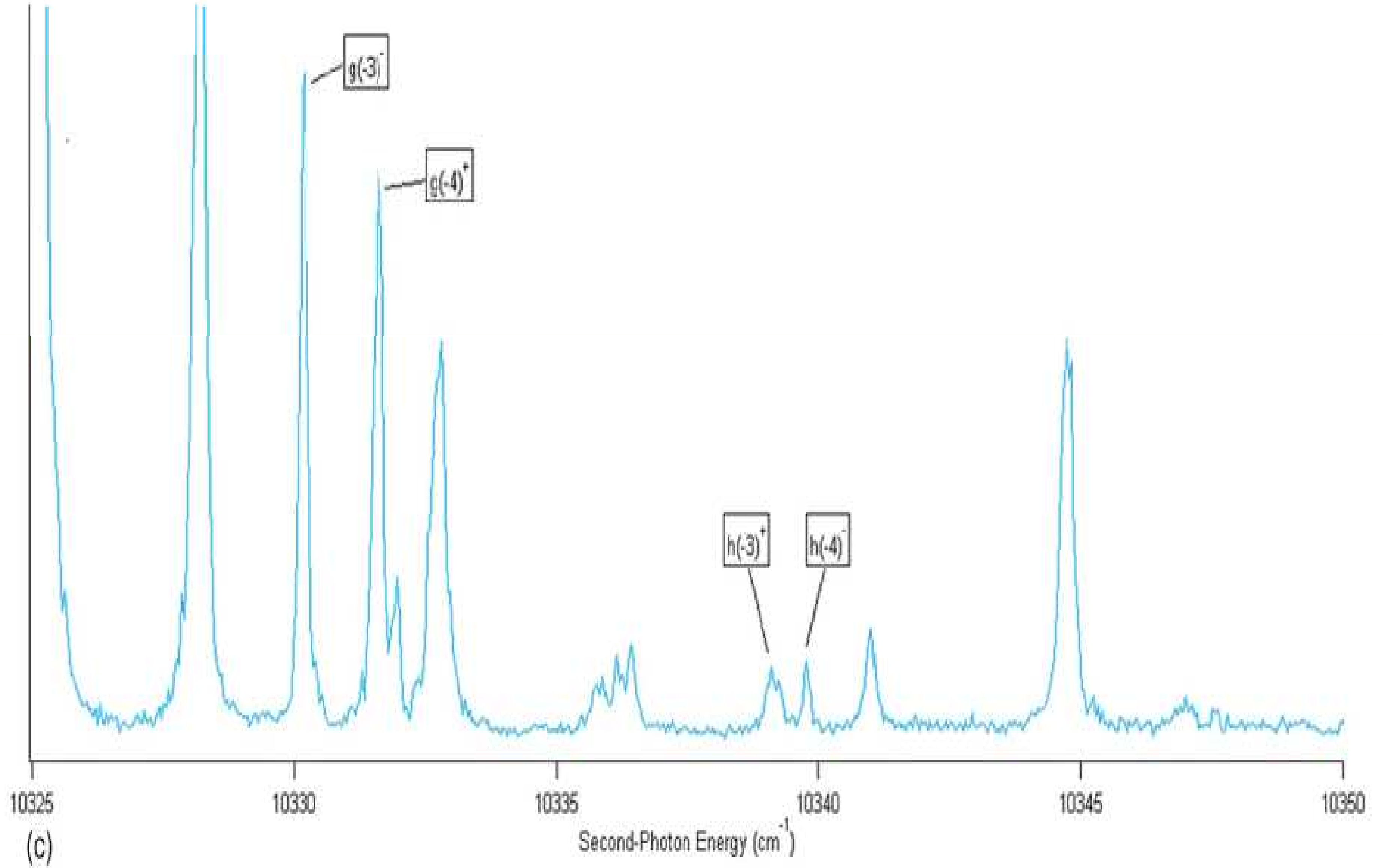
  - Ion-Core Multipole Moments and Polarizability
- Describes All Nonpenetrating $\ell$
  - $3<\ell<n-1$

# Nonpenetrating States Live Near Integer n*

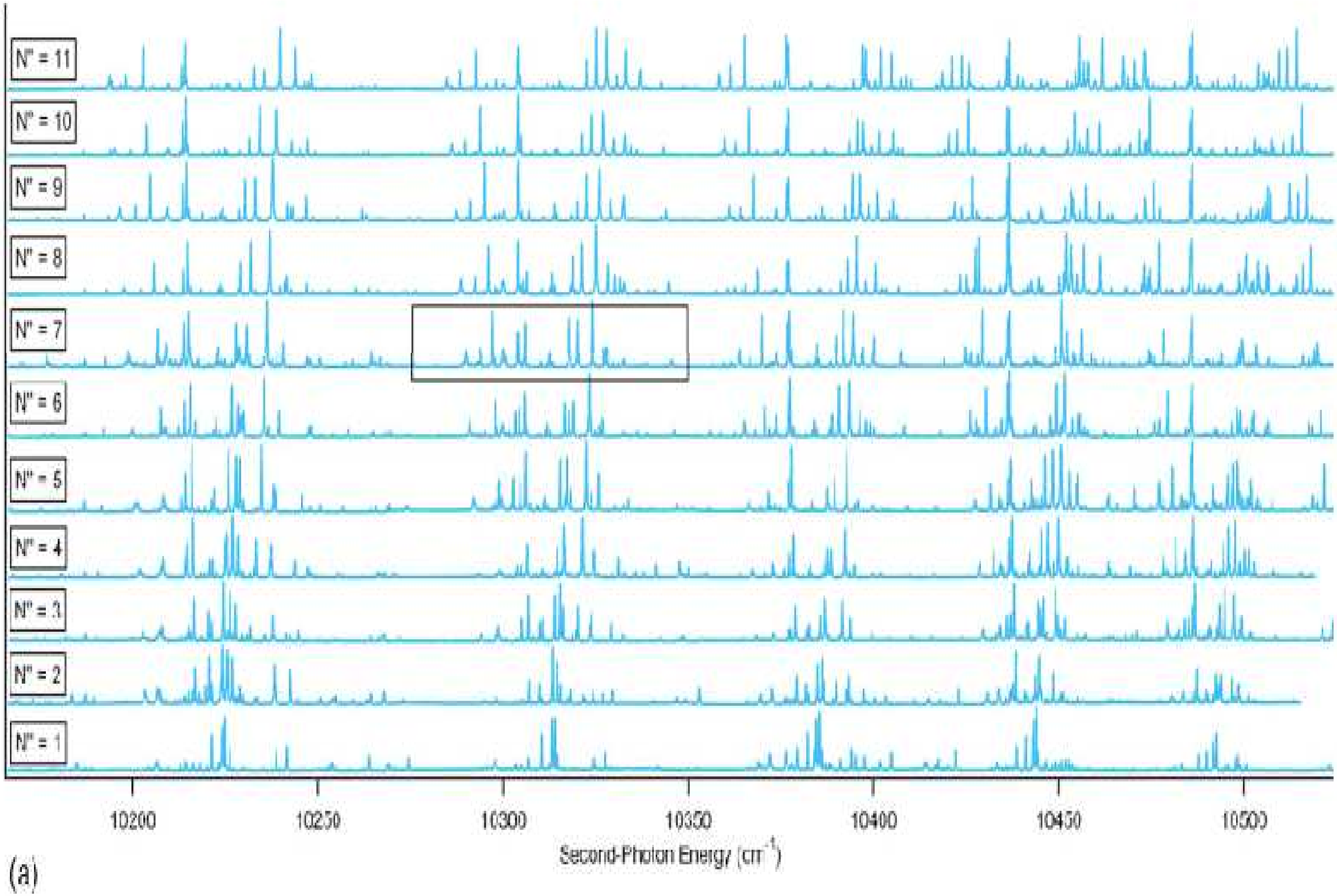



(b)

# High Resolution Detective Work Required



# Nonpenetrating States:
# Stacked Plot for $N$, $N^+$ Assignment



# Pattern-Forming Quantum Number

$$\mathbf{H}^{ROT} = B(\mathbf{N} - \ell)^2$$
$$= B\Big[N(N+1) - \lambda^2 + \ell(\ell+1) - \lambda^2 + \underbrace{(\mathbf{N}^+\ell^- + \mathbf{N}^-\ell^+)}_{\ell\text{-Uncoupling}}\Big]$$

**Case (b)**

$$\mathbf{H}^{ROT} = B(\mathbf{N}^+)^2 = BN^+(N^+ + 1)$$

$$N^+ = N - \ell_R \qquad (\ell_{\mathrm{R}} \text{ is projection of } l \text{ on } \mathbf{N}^+)$$

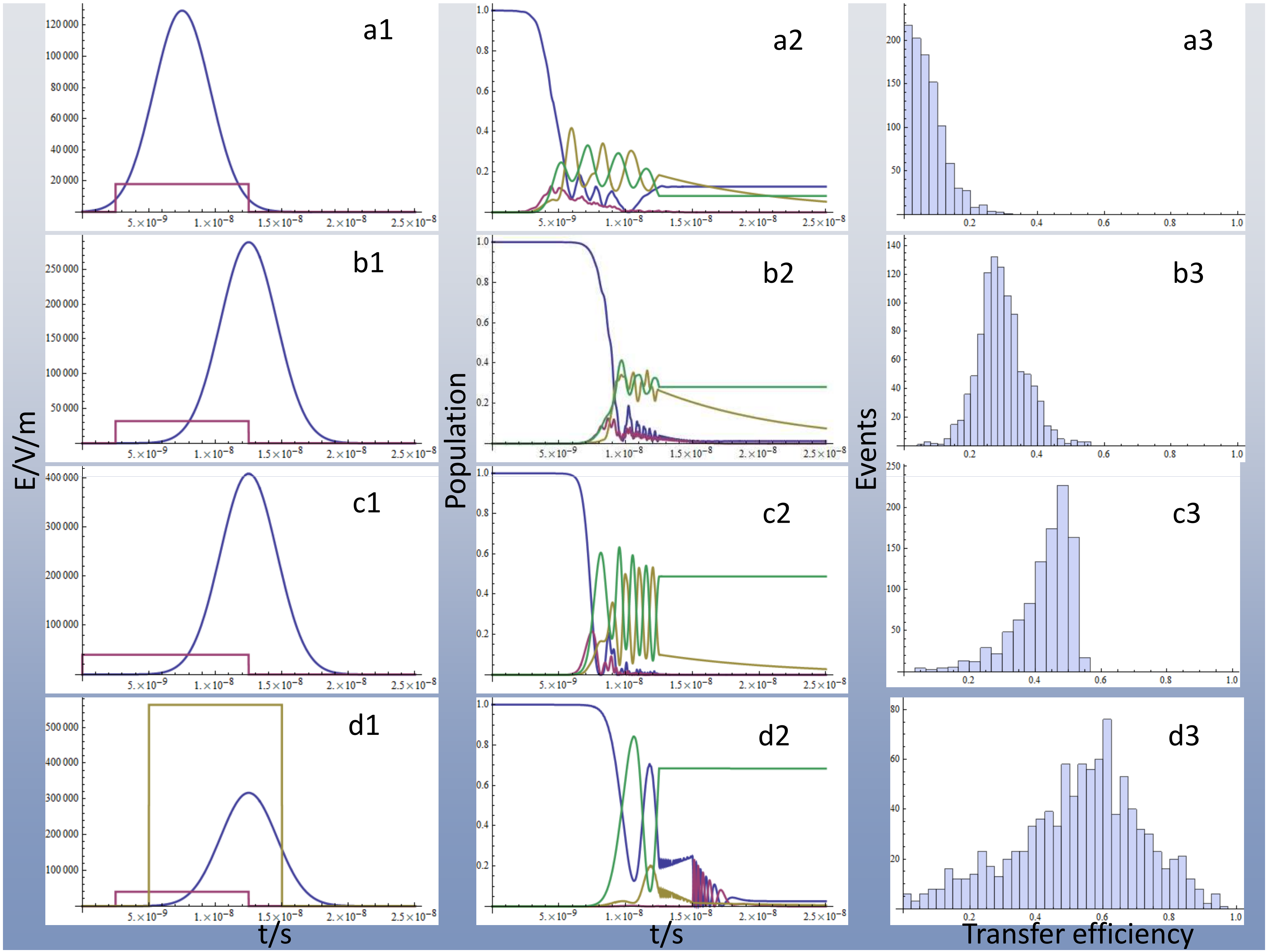
$$\mathbf{H}^{ROT} = B(N - \ell_R)(N - \ell_R + 1)$$
$$= B\Big[N(N+1) - \underbrace{2\ell_R N}_{\text{Anomalous } B_{eff}} + \ell_R^2 - \ell_R\Big]$$

**Case (d)**

*N* Determined From Combination Differences

Plot $E^{ROT}$ - $BN(N+1)$ vs. $N$

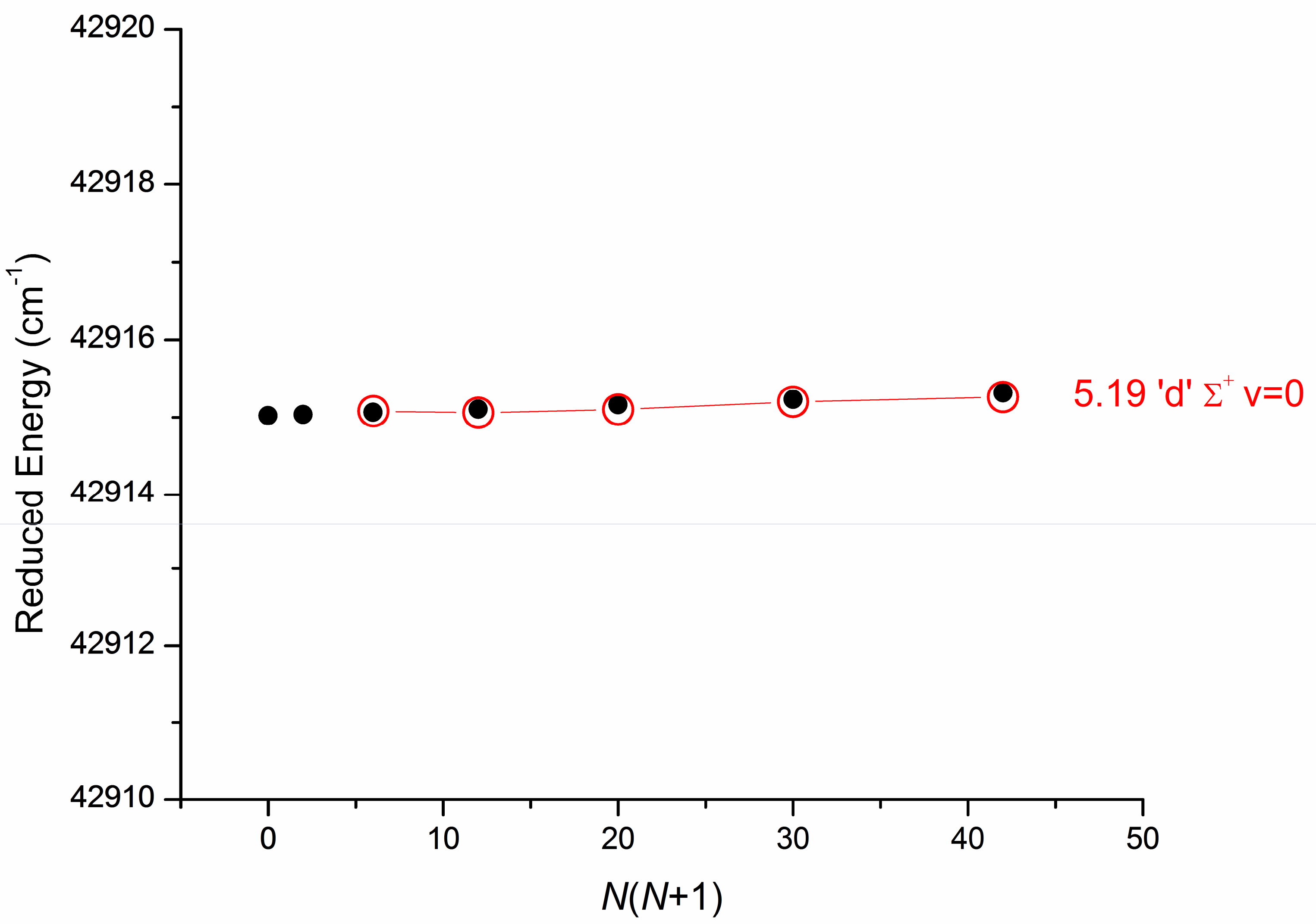
Slope is $-2B\ell_R$; Determines $N^+$


a1
a2
a3
b1
b2
b3
c1
c2
c3
d1
d2
d3
E/V/m
Population
Events
t/s
t/s
Transfer efficiency

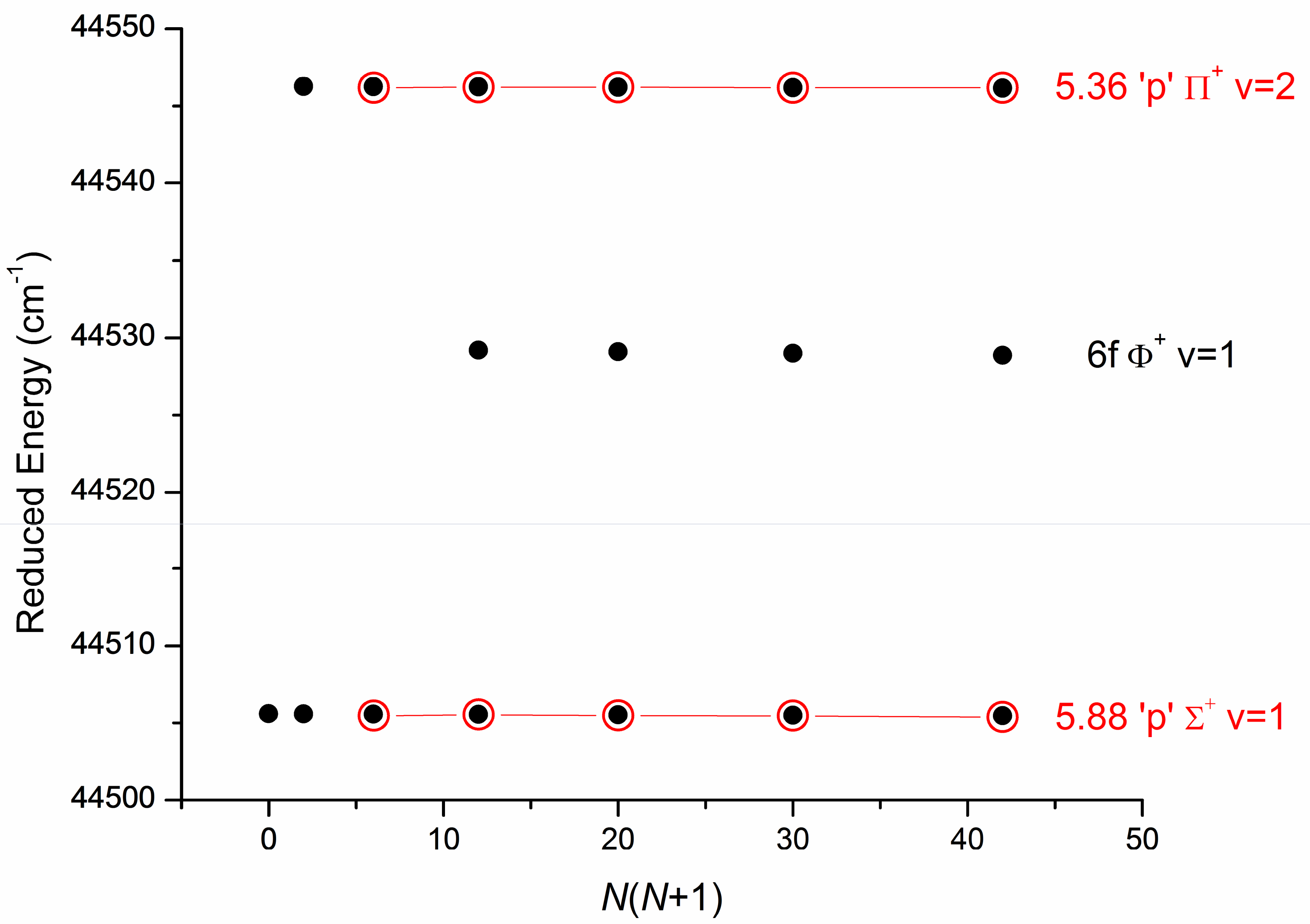
# Pure Electronic Spectroscopy

- Transitions between core-nonpenetrating states
- Integer n*
- Intra-core dynamical processes turned off
- ng to (n+1)h transitions
  - 1000 Debye transition moment
  - No torque, no impulse: $\Delta v^{+}=0$, $\Delta J^{+}=0$

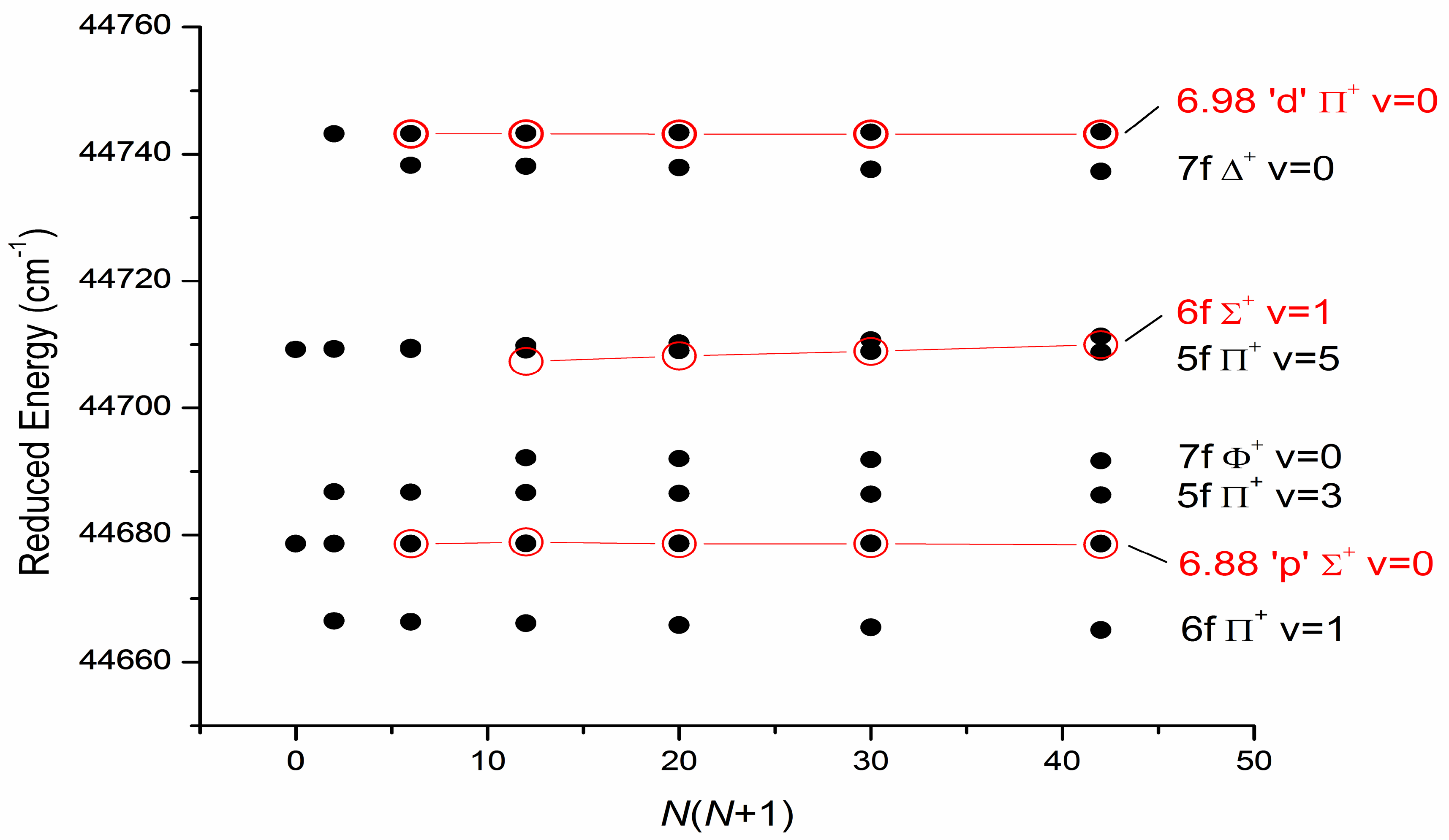
    Need very high resolution to sample ion-core multipole moments and polarizability
  - Long-range model



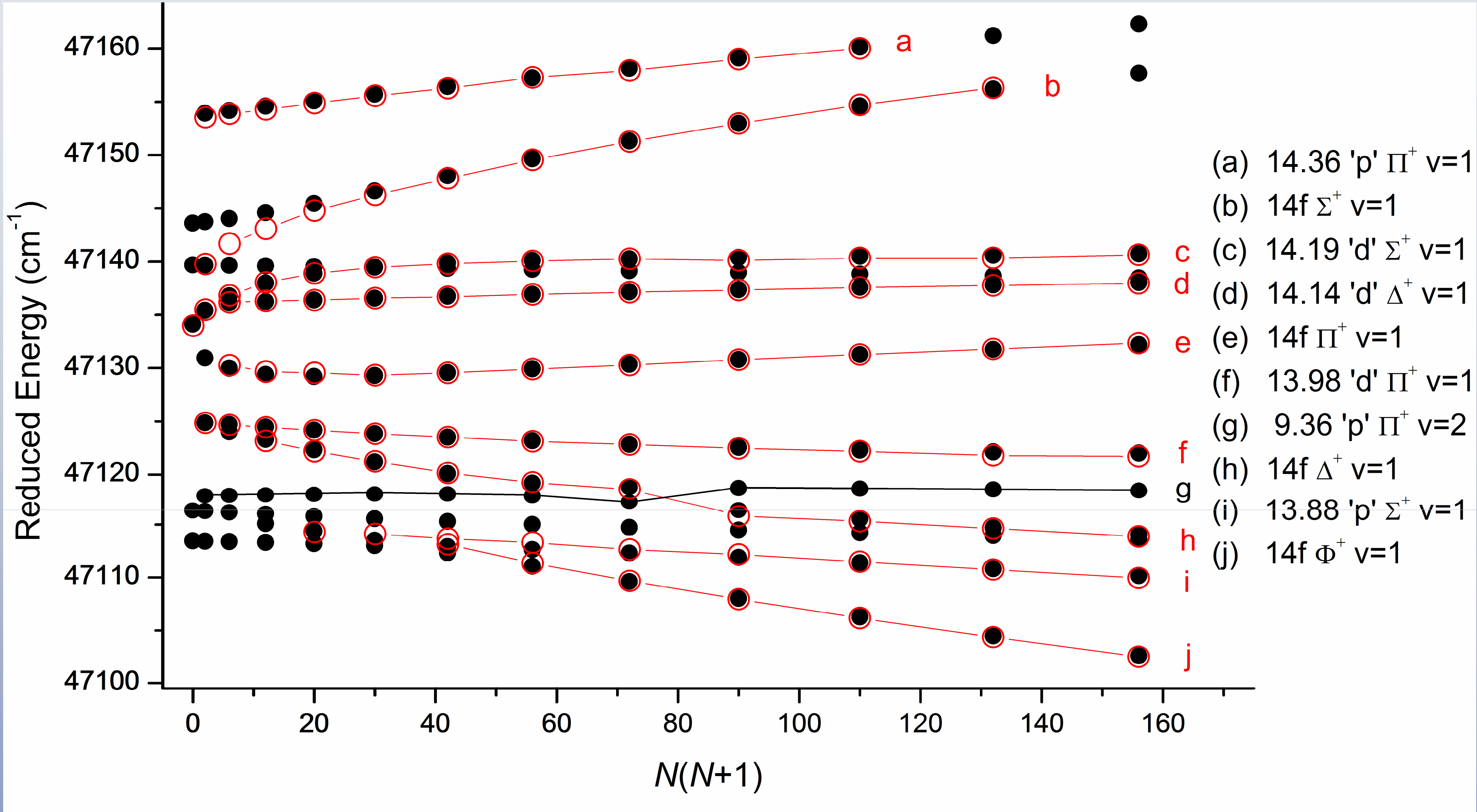

Quality of fit near $n^*$ = 5.0, where vibronic states tend to be well-separated



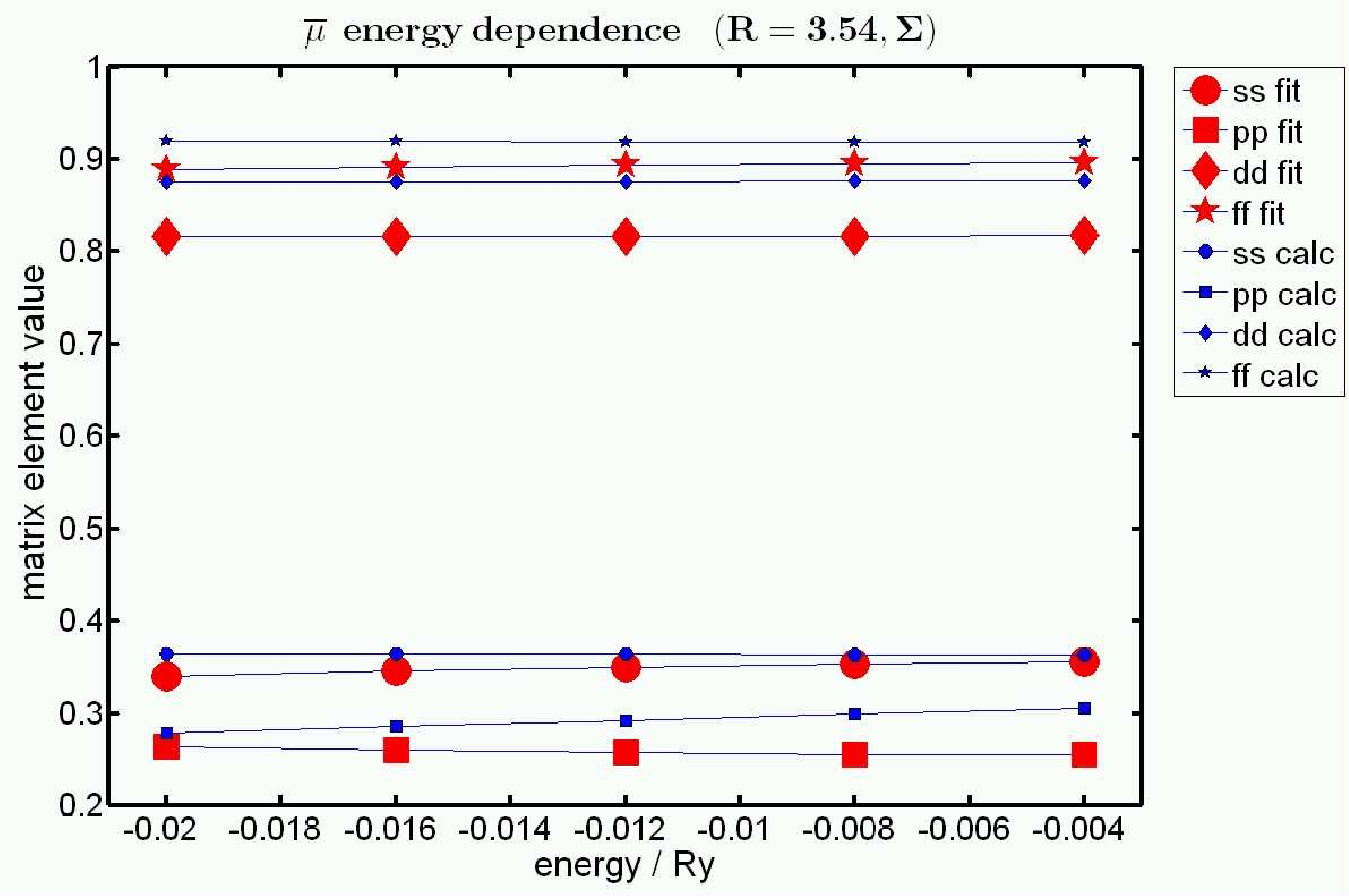

Quality of fit for vibrationally-excited levels with low *n**.



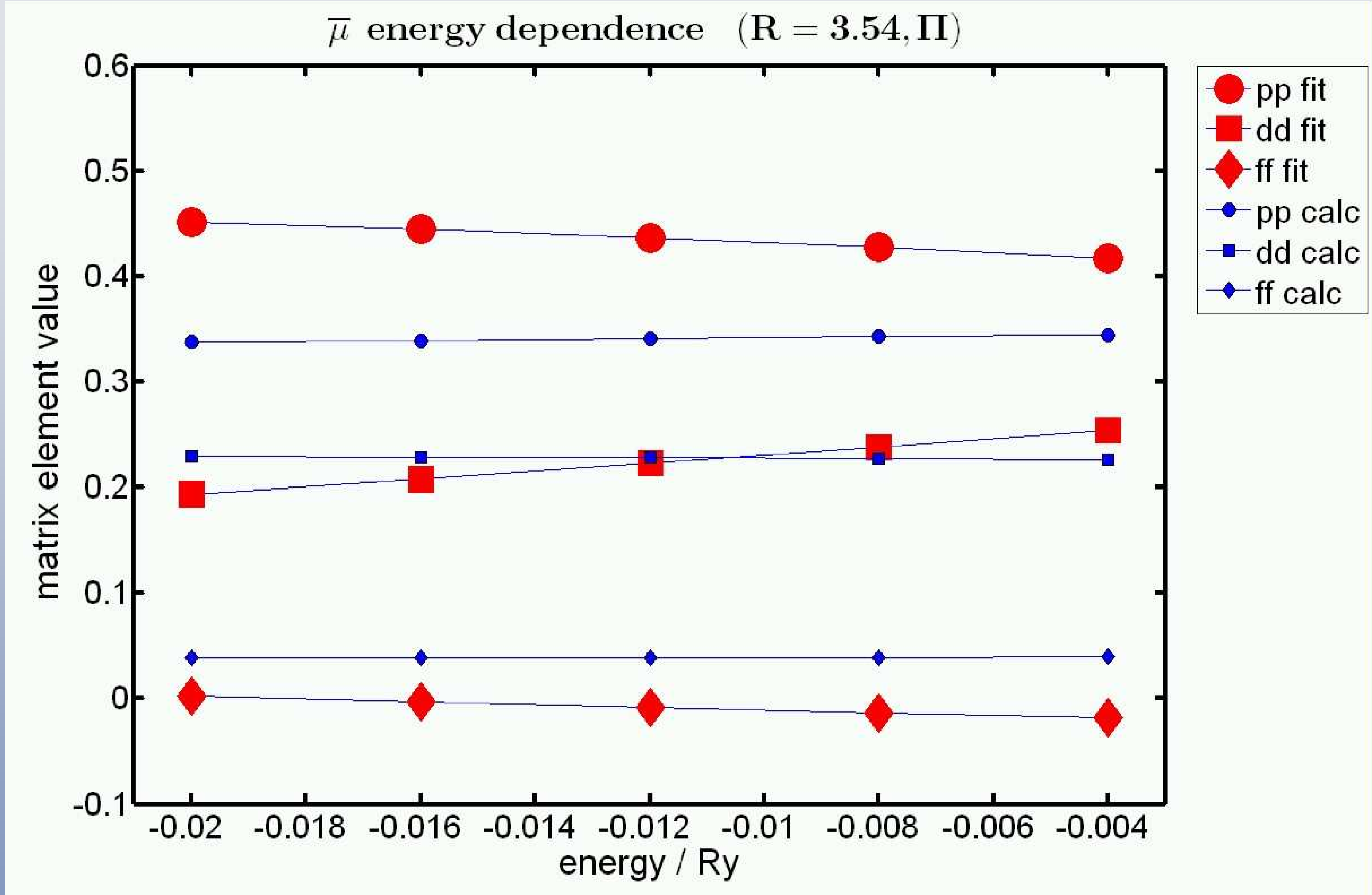

Quality of fit in the vicinity of n* = 7.0. Vibronic states at this energy are interleaved. Here, the classical period of electronic motion (proportional to $n^{*3}$) is approximately equal to the classical period of vibrational motion. Vibronic perturbations are frequent.



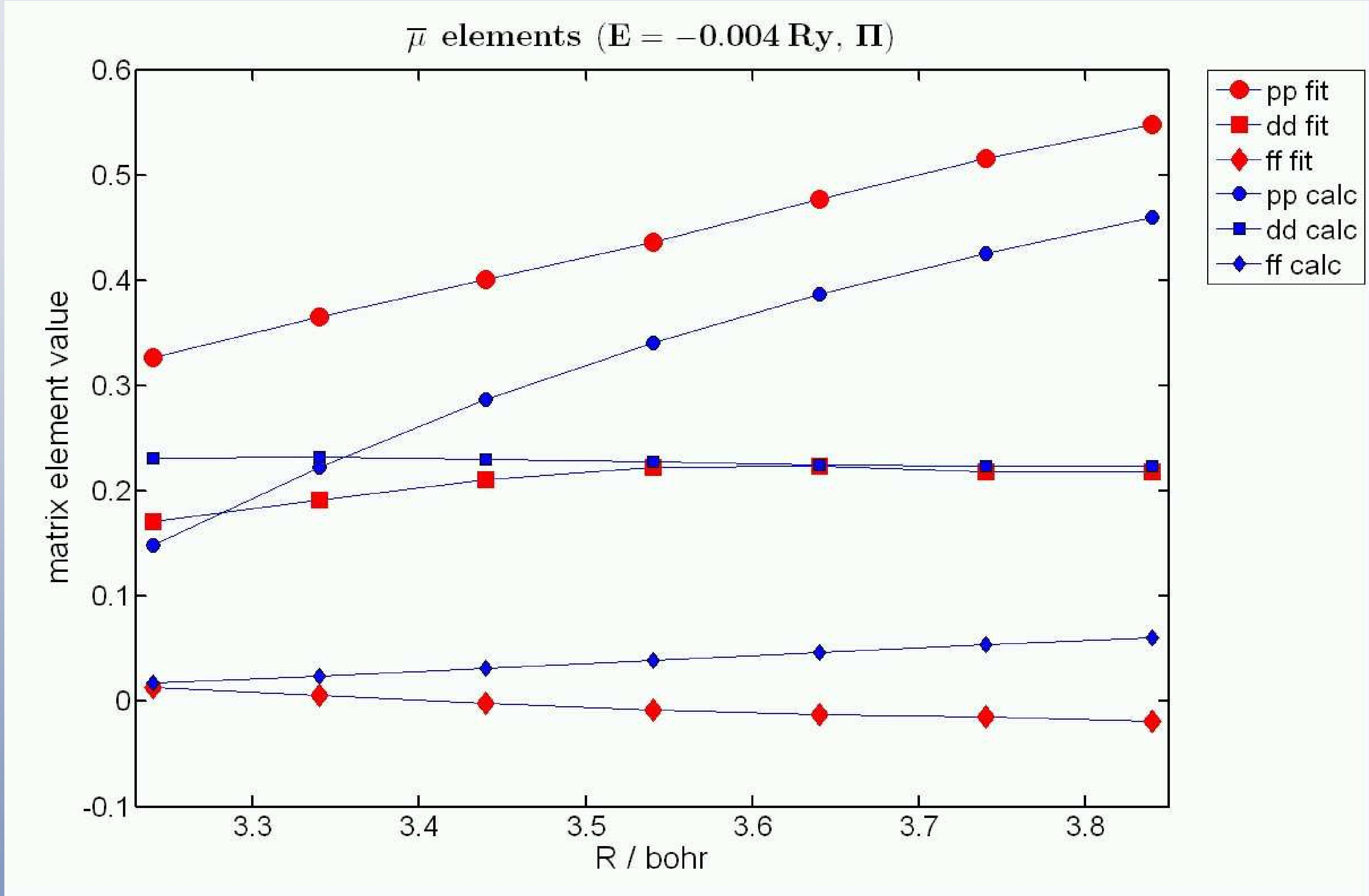

Quality of fit in the vicinity of n* = 14.0. At this energy, the electronic energy level spacing is much smaller than the vibrational spacing, but still larger than the rotational spacing of the ion core energy levels. Vibronic perturbations are uncommon, but rotational (inhomogeneous) perturbations become increasingly frequent. An avoided crossing can be seen between 14f $\Delta^+$ v=1 and 9.36 ‘p’ $\Pi^+$ v=2.



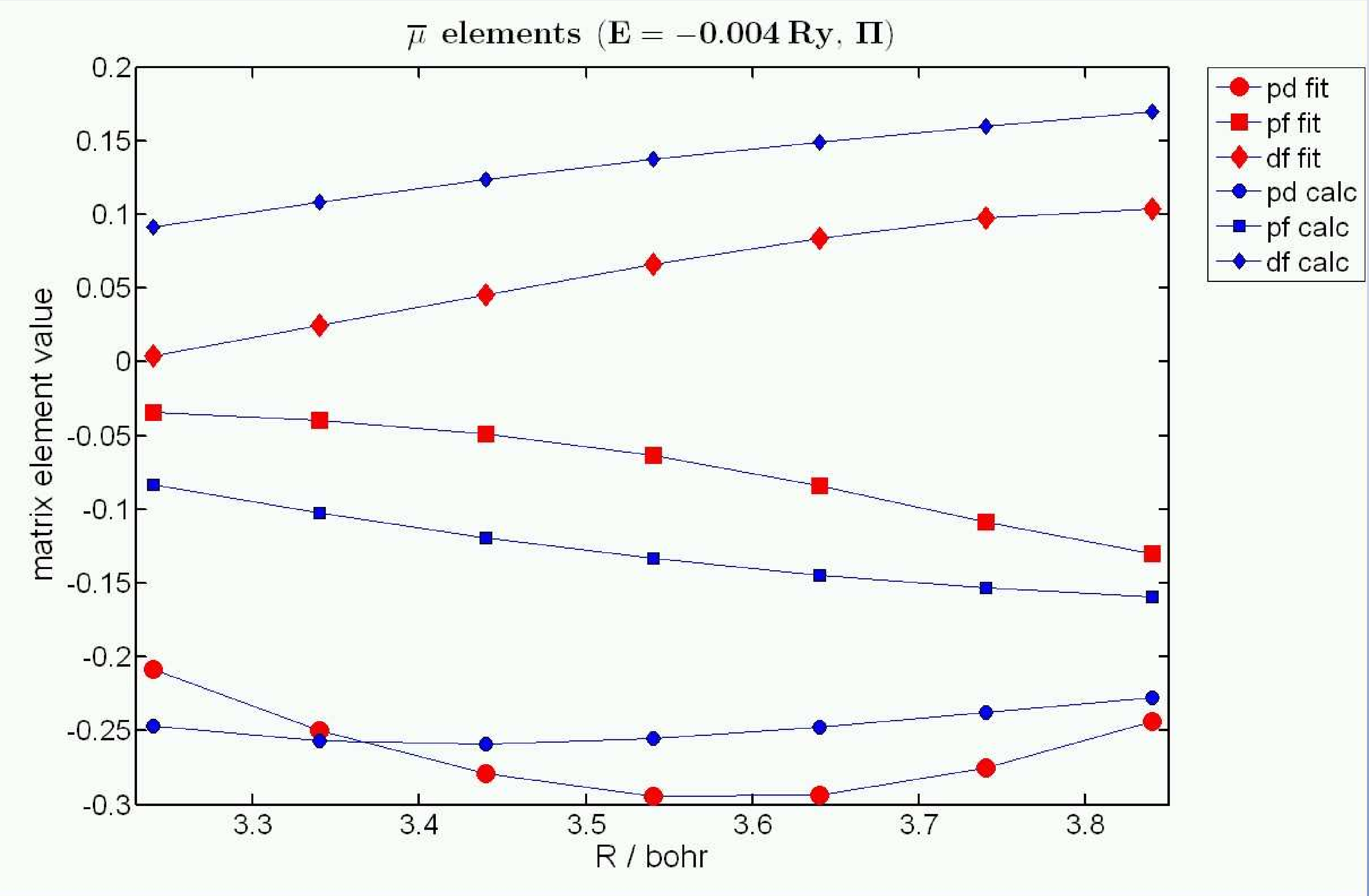

Fitted and computed quantum defects for Σ symmetry, at $R = R_e^+ = 3.54$ $a_0$.




Quantum defects for $\Pi$ symmetry, at $R = R_e^+ = 3.54\ a_0$.




Quantum defects for Π symmetry, at *E* = - 0.004 Ry, diagonal elements.




Quantum defects for $\Pi$ symmetry, at $E$ = - 0.004 Ry, off-diagonal elements.

# CaF: The “Alkali Atom of Diatomic Molecules” with a Highly Polar Ion-Core

**Multipole Moments (atomic units):**

| | μ | Q |
|---|---|---|
| CaF+ | 0 | 11.3 |
| NO+ | 0 | ~0.74 |

Center of Charge Coordinates

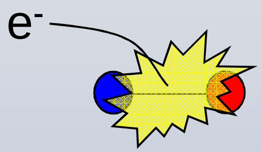
| | μ | Q |
|---|---|---|
| CaF+ | 3.52 | 8.96 |
| NO+ | 0.15 | 0.74 |

Center of Mass Coordinates

**$CaF^+$ (center of mass) dipole moment: 8.9 Debye**
**CaF $v$ =0 to $v^+$=0 Ionization Potential: ~47,000 $cm^{-1}$**
**CaF $v$ =0 to Ca($^1S$) + F($^2P$) Dissociation Energy: ~44,200 $cm^{-1}$ ($n^*$≈6)**
**Separated-Atom Excited States:** Ca 4s4p $^3P$ at **>15,000 $cm^{-1}$**

# Classical Mechanism

Low n*: Core essentially **stationary**

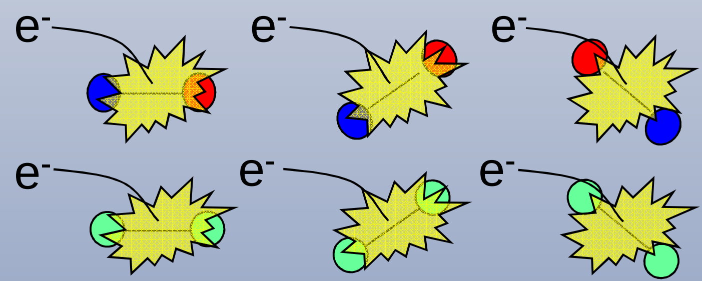



$$\tau_{Kepler} \ll \tau_{Rot}$$

High n* but **not resonant:**

**Odd-rank** electrostatic interactions
*average toward zero*

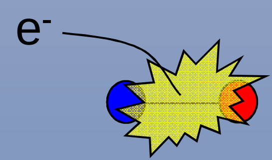
**Even-rank** interactions *persist*




$$n \cdot \tau_{Rot} < \tau_{Kepler} < (n+1) \cdot \tau_{Rot}$$

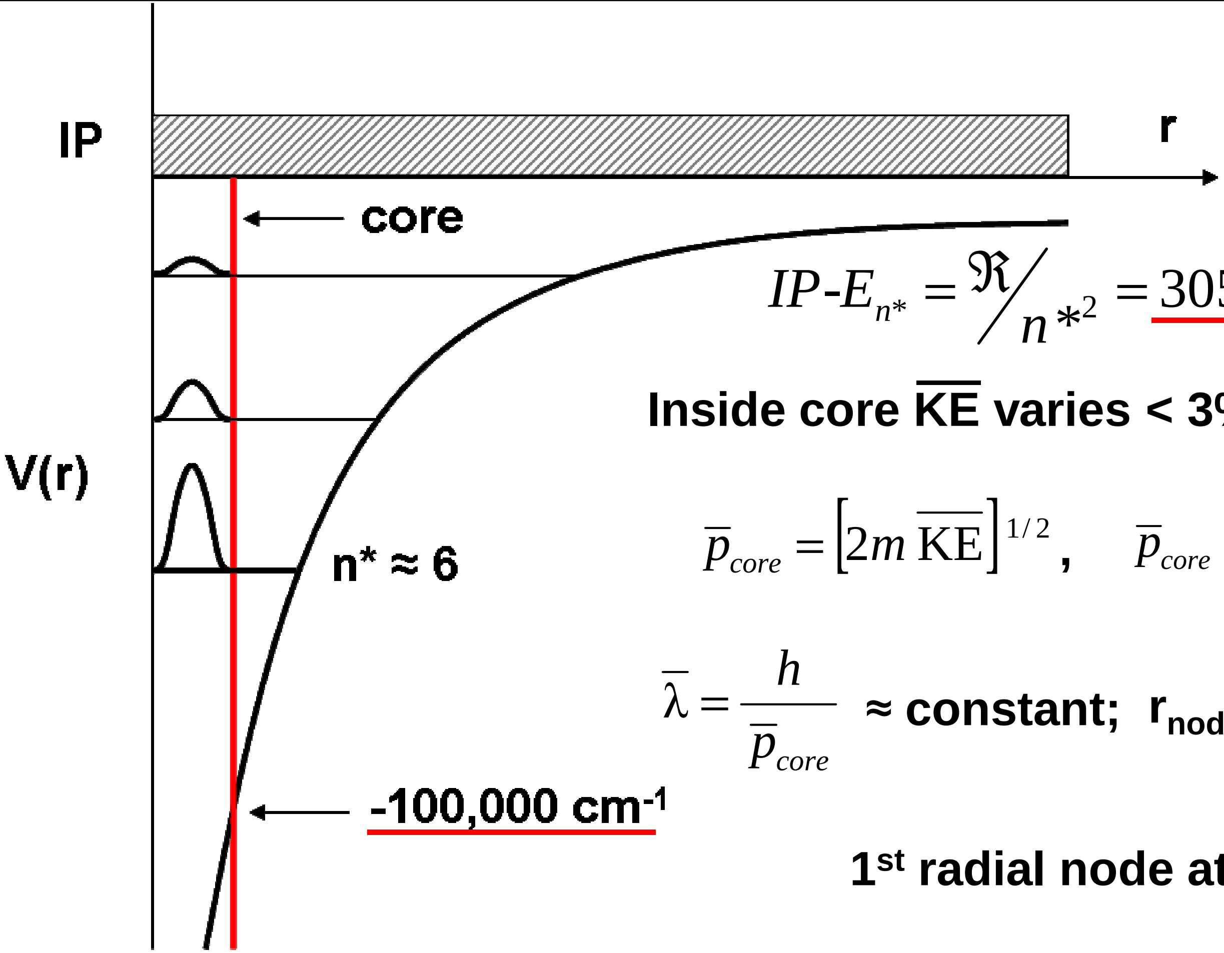
High n* but **resonant:**

Core *appears* **stationary**




$$\tau_{Kepler} = n \cdot \tau_{Rot}$$

# Physical Basis for $n^{*-3}$ Scaling (1)




$$IP\text{-}E_{n^*} = \Re / n^{*2} = \underline{3050\ \text{cm}^{-1}}\ \text{at}\ n^* = 6$$

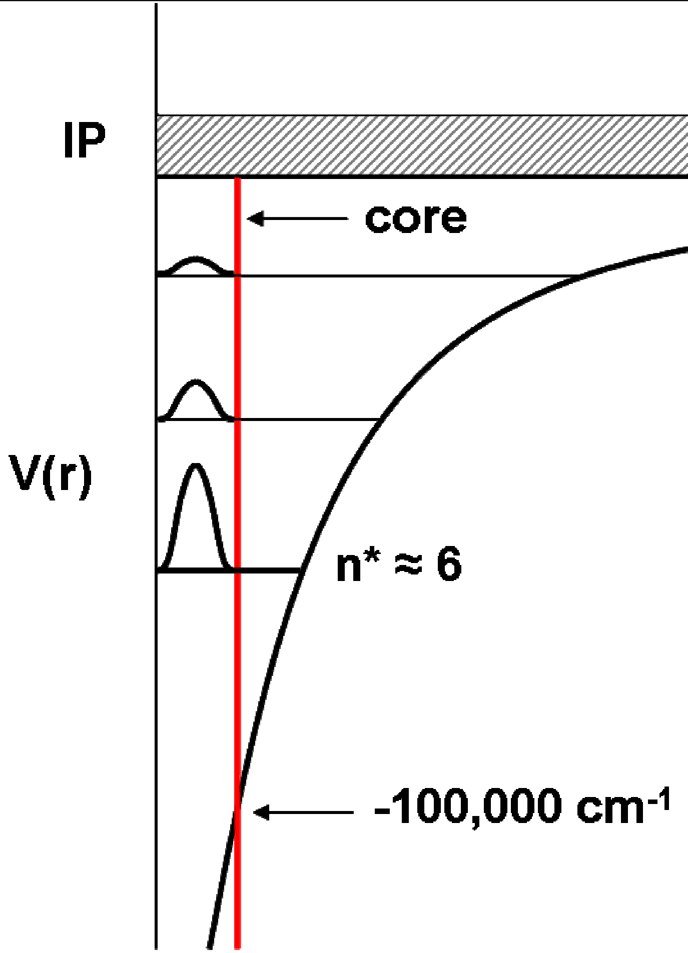
**Inside core $\overline{\text{KE}}$ varies < 3% *n** = 6 → *n** = ∞**

$$\overline{p}_{core} = \left[2m\,\overline{\text{KE}}\right]^{1/2},\quad \overline{p}_{core}$$ **varies by < 1.5%**

$$\overline{\lambda} = \frac{h}{\overline{p}_{core}}$$ **≈ constant; $r_{node}$ n*-independent, n* ≥ 6**

**1st radial node at** $r \approx \overline{\lambda}/2$

# Physical Basis for $n^{*-3}$ Scaling (2)




$$\begin{pmatrix}\text{amplitude}\\ \text{in inner}\\ \text{lobe}\end{pmatrix}^2 = \frac{\bar{\lambda}/\bar{\nu}}{\left(\frac{\text{orbit period}}{2}\right)} = \frac{\text{constant}}{n^{*3}}$$

$$\downarrow$$

**Kepler period:** $$\frac{h}{E_{n^*+\frac{1}{2}} - E_{n^*-\frac{1}{2}}} = \frac{h}{2c\mathfrak{R}/n^{*3}}$$

**Inner lobe amplitude ~ $n^{*-3/2}$**

# Mulliken's Rule

"**Ontogeny recapitulates phylogeny**" (E. Haeckel, ~1900). The growth of the organism from a single cell to adult mirrors the evolutionary development of the species.

The innermost lobes of a Rydberg orbital remain invariant (shapes, positions of nodes) for all members of a Rydberg series, aside from an $n^{*-3/2}$ amplitude scale factor.

The low-n* terminus state of a Rydberg series is *explained* by LCAO-MO (bonding/antibonding) or LFT (shielding).

Most dynamics is *encoded* in the innermost lobe.

Basis for n*-*scaling* of everything in Rydberg-land.

# Franck-Condon Factors

$X^+\ {}^1\Sigma^+$ $v^+ \rightarrow$

$D\ {}^2\Sigma^+$ $v$

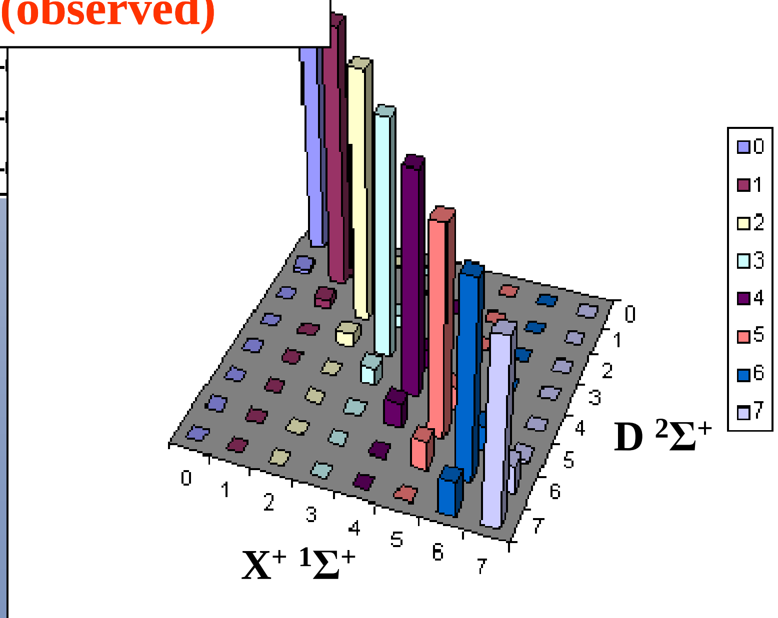
| | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|---|
| 0 | 9.83E-01 | 1.68E-02 | 2.66E-05 | 4.96E-06 | 7.66E-07 | 5.51E-08 | 3.20E-09 | 1.63E-10 |
| 1 | 1.65E-02 | 9.49E-01 | 3.46E-02 | 9.61E-05 | 1.90E-05 | 3.83E-06 | 3.32E-07 | 2.23E-08 |
| 2 | 3.76E-04 | 3.32E-02 | 9.13E-01 | 5.32E-02 | 2.30E-04 | [illegible] | [illegible] | [illegible] |
| 3 | [illegible] | 1.13E-03 | 4.99E-02 | 8.76E-01 | 7.25E-02 | [illegible] | [illegible] | [illegible] |
| 4 | [illegible] | 4.43E-06 | 2.46E-[illegible] | [illegible] | [illegible]7E-01 | [illegible] | [illegible] | [illegible] |
| 5 | [illegible] | 5.35E-07 | 1.25E-[illegible] | [illegible] | [illegible]2E-02 | 7.97E-[illegible] | [illegible] | [illegible] |
| 6 | [illegible] | [illegible] | [illegible] | [illegible] | [illegible]7E-03 | 9.96E-[illegible] | [illegible] | [illegible] |
| 7 | [illegible] | [illegible] | [illegible]E-08 | 4.18E-06 | 5.56E-05 | 9.71E-[illegible] | [illegible] | [illegible] |

Strongly Allowed (observed)

Weakly Allowed (observed)

Forbidden (observed)

Strongly Forbidden (observed)



# FID Contains Ca 34.13p-33.67s: Polarized by 500 MHz Chirp