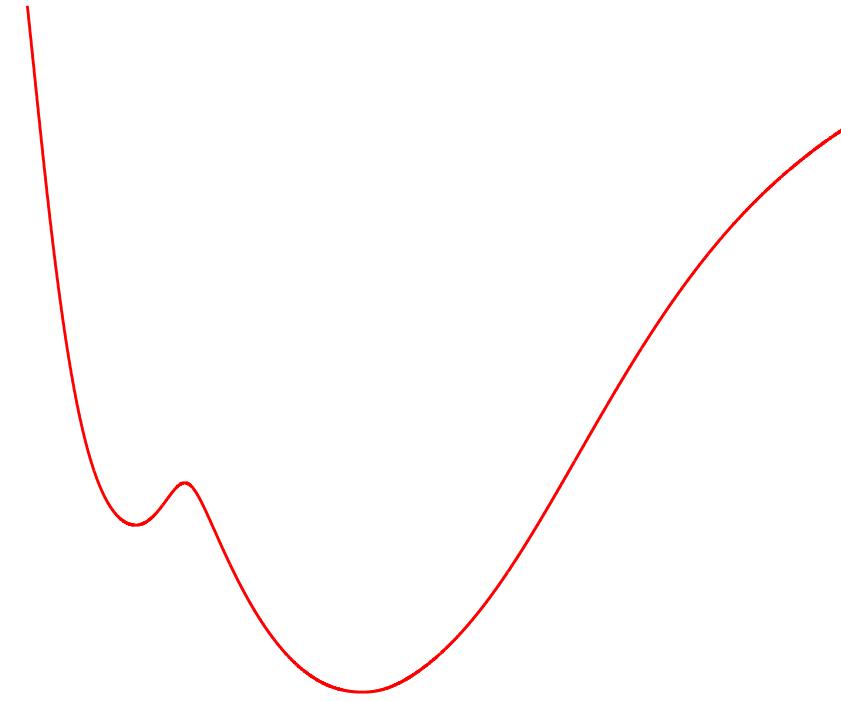


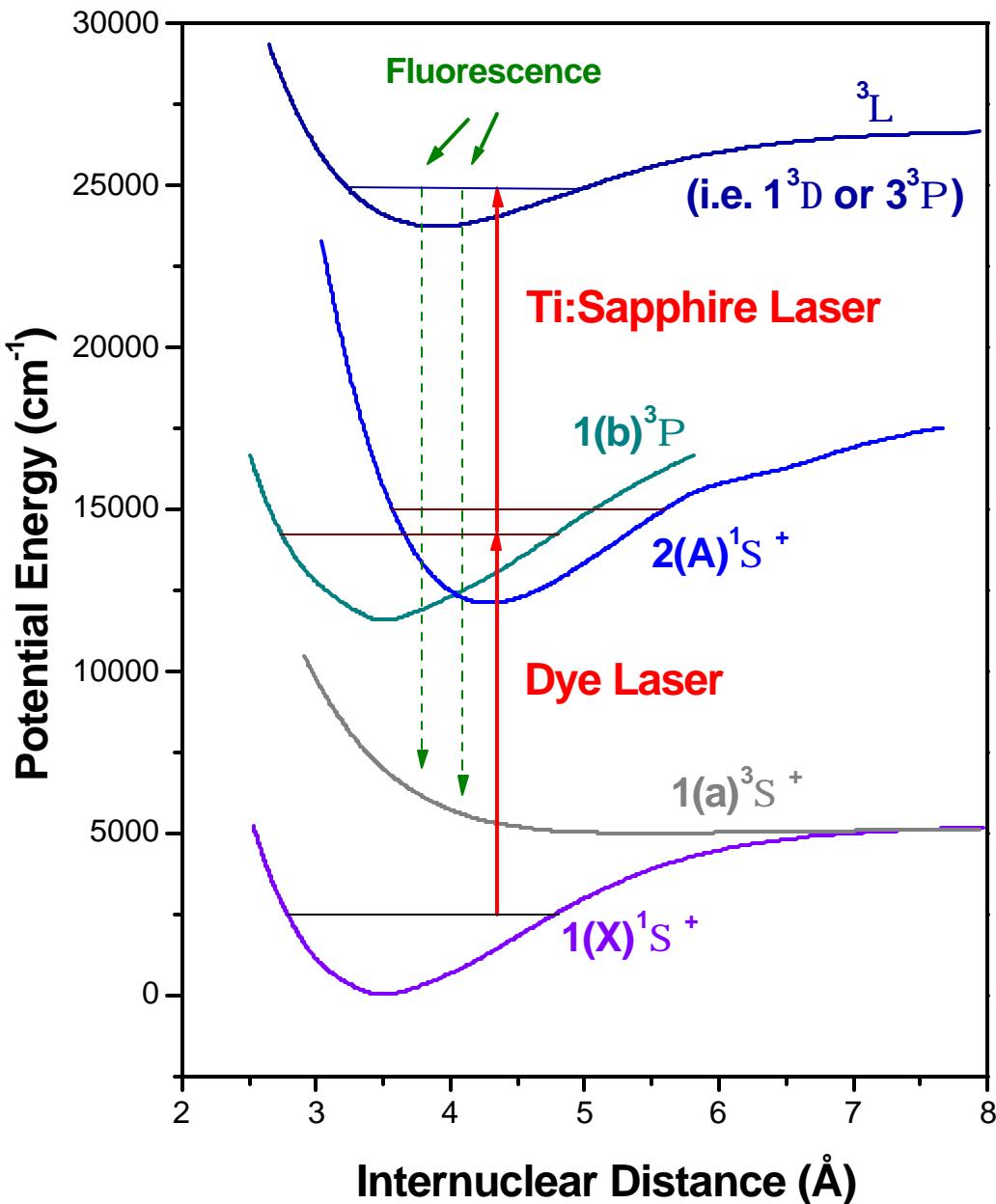
# Theoretical Studies of the NaK $3^3\Pi$ Double Minimum State



R. Miles, A. Wilkins, L. Morgus, J. Huennekens, A. P. Hickman.  
Department of Physics, Lehigh University

work supported by NSF and by the USDE GAANN Fellowship program

# Perturbation Facilitated Optical-Optical Double Resonance (PFOODR) Technique

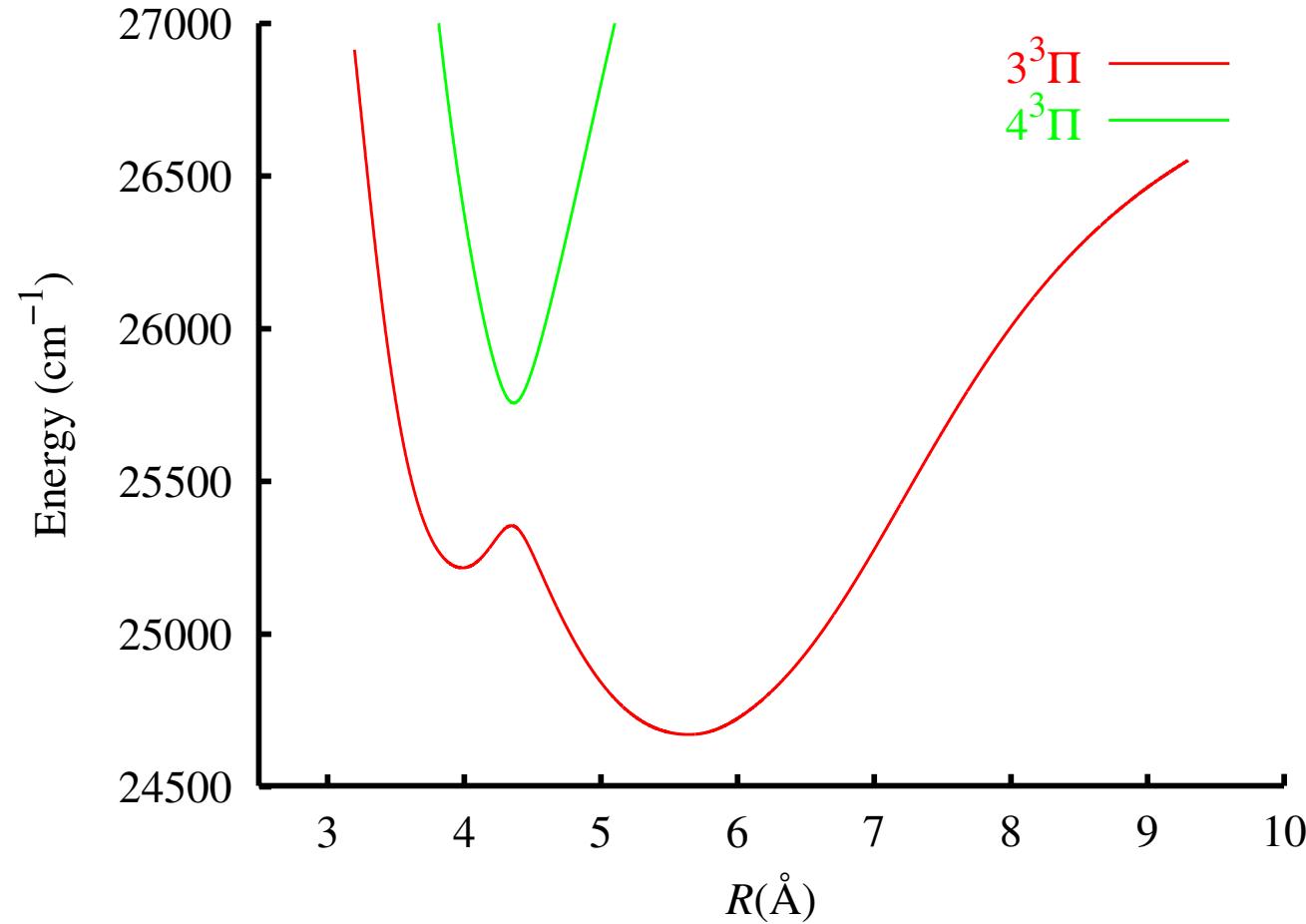


Selection Rules

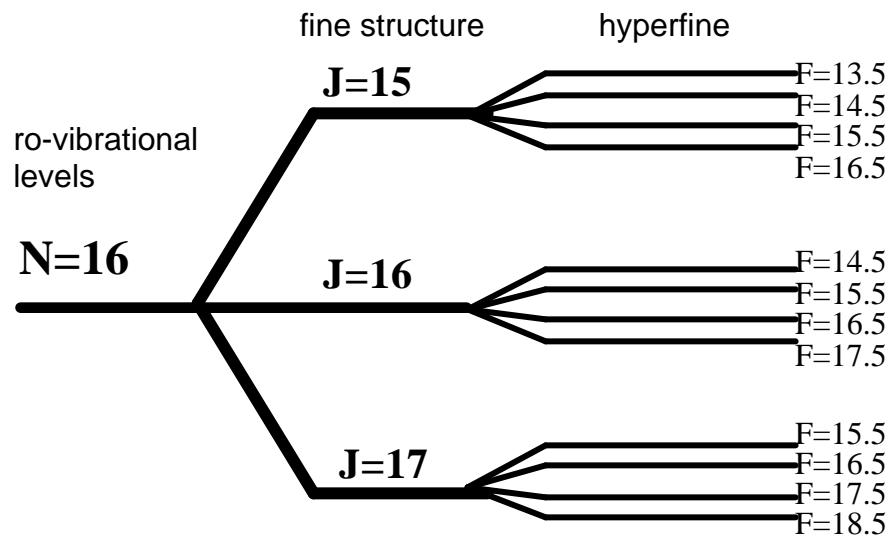
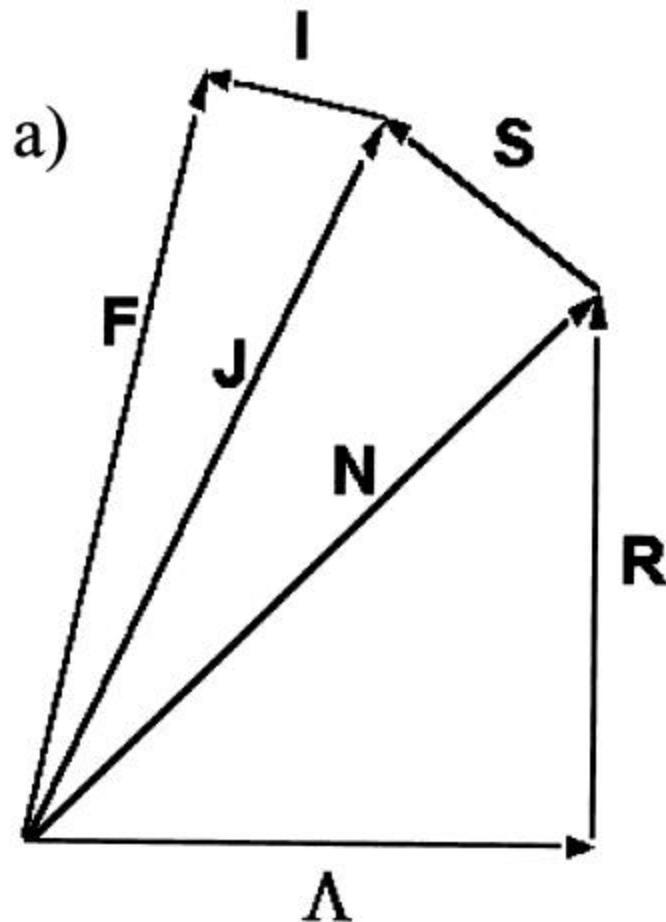
$$\Delta \Lambda = -1, 0, +1$$

$$\Delta S = 0$$

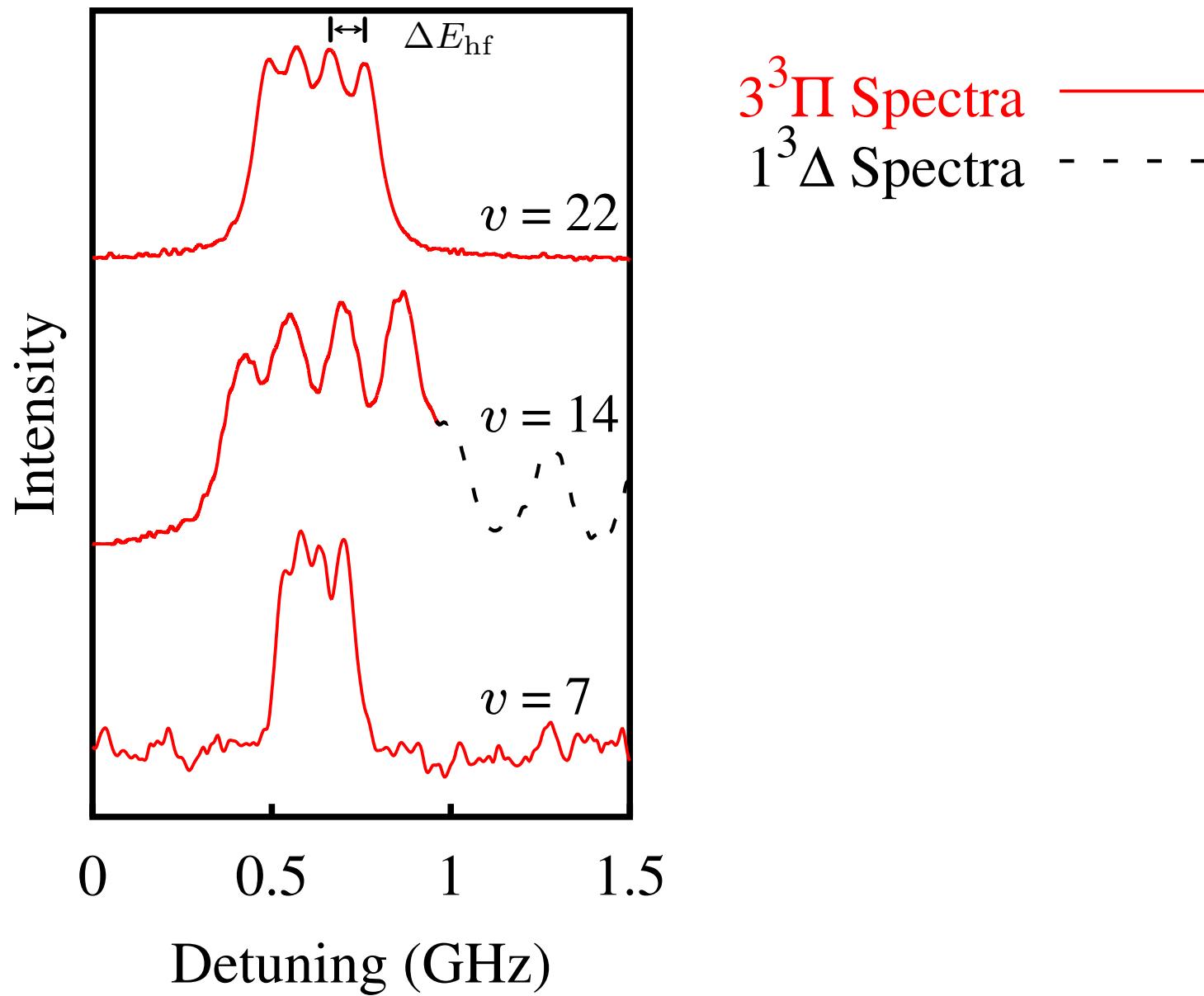
# The $3^3\Pi$ and $4^3\Pi$ Potential Curves



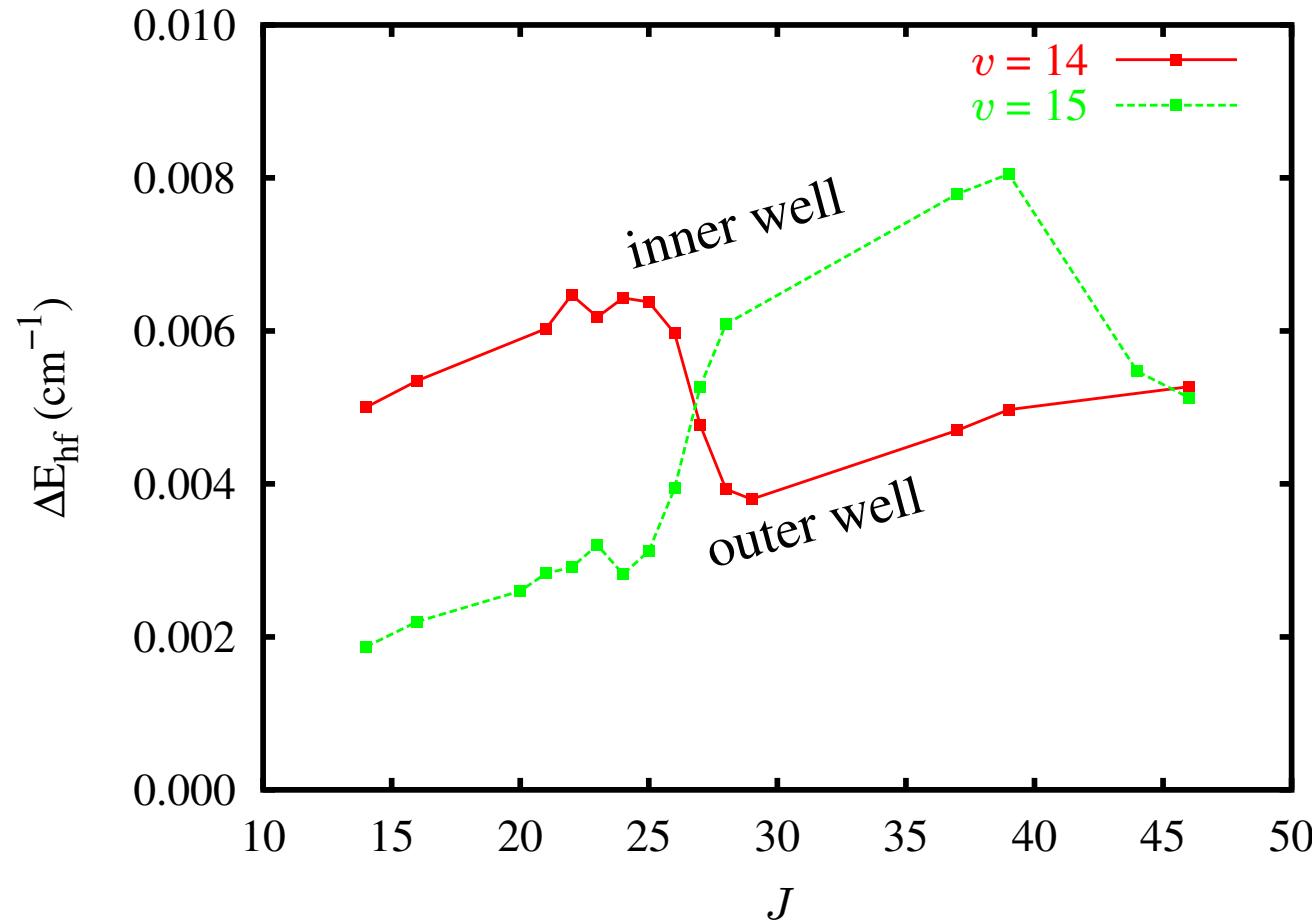
# Hyperfine Structure



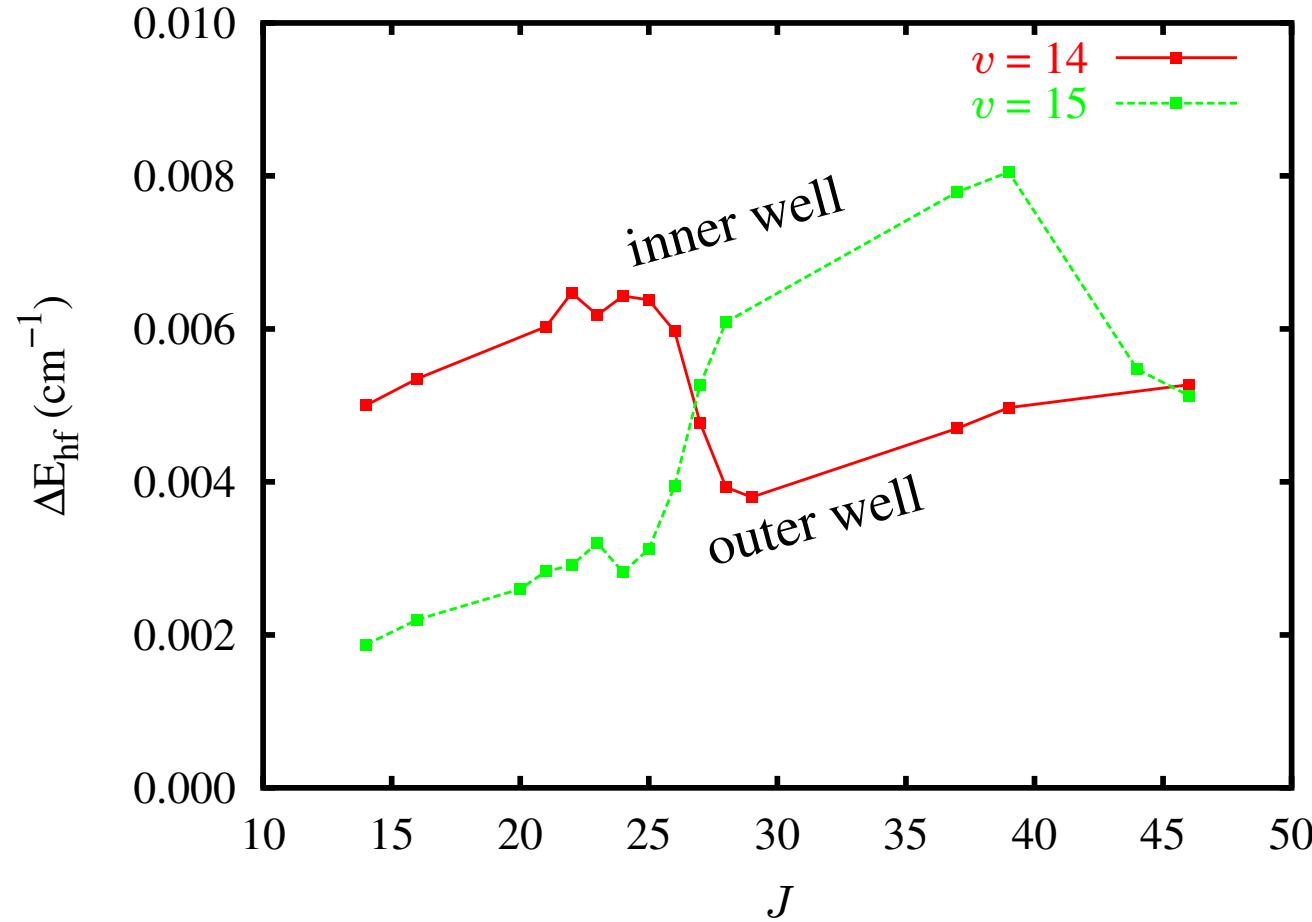
# Hyperfine Structure: $J = 14$



# $\Delta E_{\text{hf}}(v, J)$ vs. $J$



# $\Delta E_{\text{hf}}(v, J)$ vs. $J$



We can explain this theoretically.

# DMM Fit for $3^3\Pi$ and $4^3\Pi$ States

The diabatic mixing model (DMM) fit:

- an analytic diabatic Hamiltonian

# DMM Fit for $3^3\Pi$ and $4^3\Pi$ States

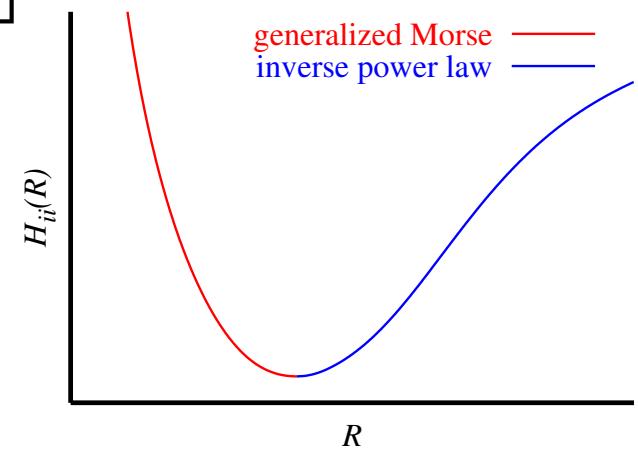
The diabatic mixing model (DMM) fit:

- an analytic diabatic Hamiltonian

$$\mathbf{H}_{\text{diabatic}}(R) = \begin{bmatrix} H_{11}(R) & H_{12}(R) \\ H_{12}(R) & H_{22}(R) \end{bmatrix}$$

$$H_{ii}(R) = \begin{cases} V_1^{(i)}(R) & \text{if } R < R_e^{(i)} \\ V_2^{(i)}(R) & \text{if } R \geq R_e^{(i)}, \end{cases}$$

$$H_{12}(R) = A \exp(-\gamma(R - R_0)^2)$$



# DMM Fit for $3^3\Pi$ and $4^3\Pi$ States

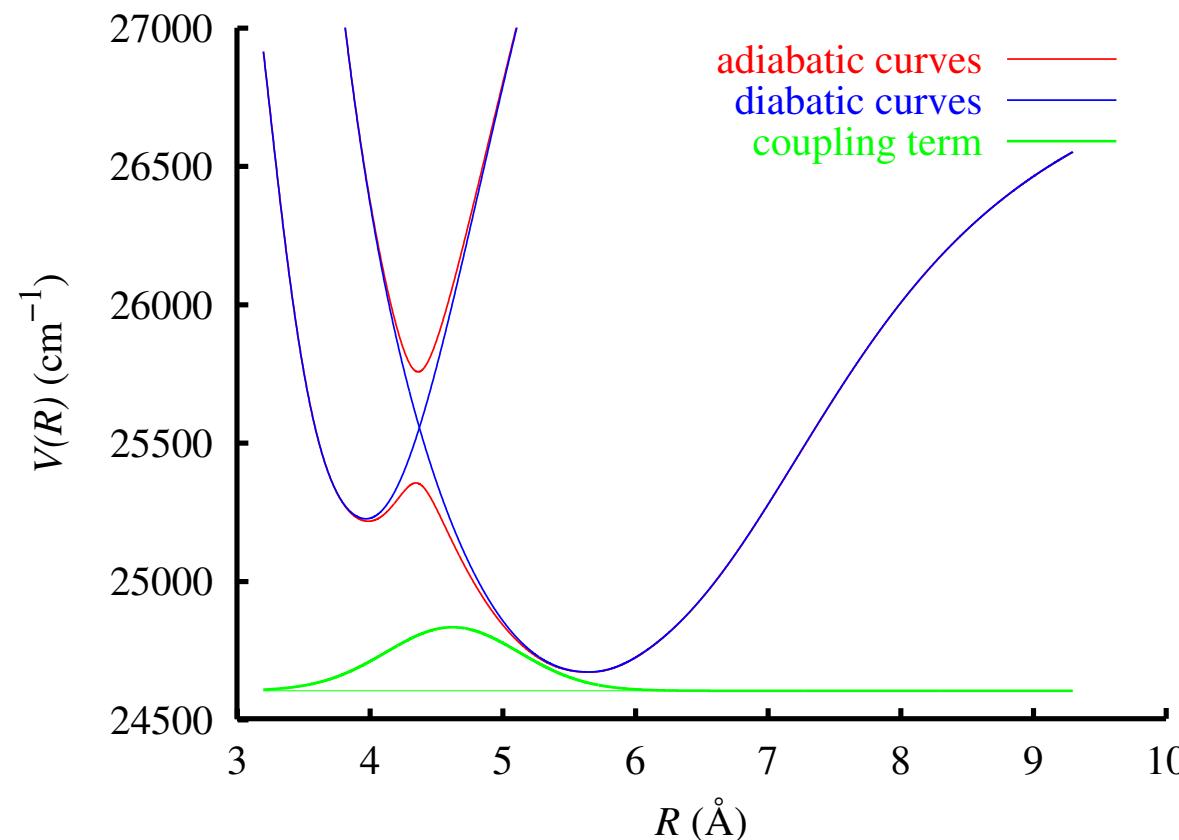
The diabatic mixing model (DMM) fit:

- an analytic diabatic Hamiltonian
- non-linear least squares fit

# DMM Fit for $3^3\Pi$ and $4^3\Pi$ States

The diabatic mixing model (DMM) fit:

- an analytic diabatic Hamiltonian
- non-linear least squares fit
- Results:

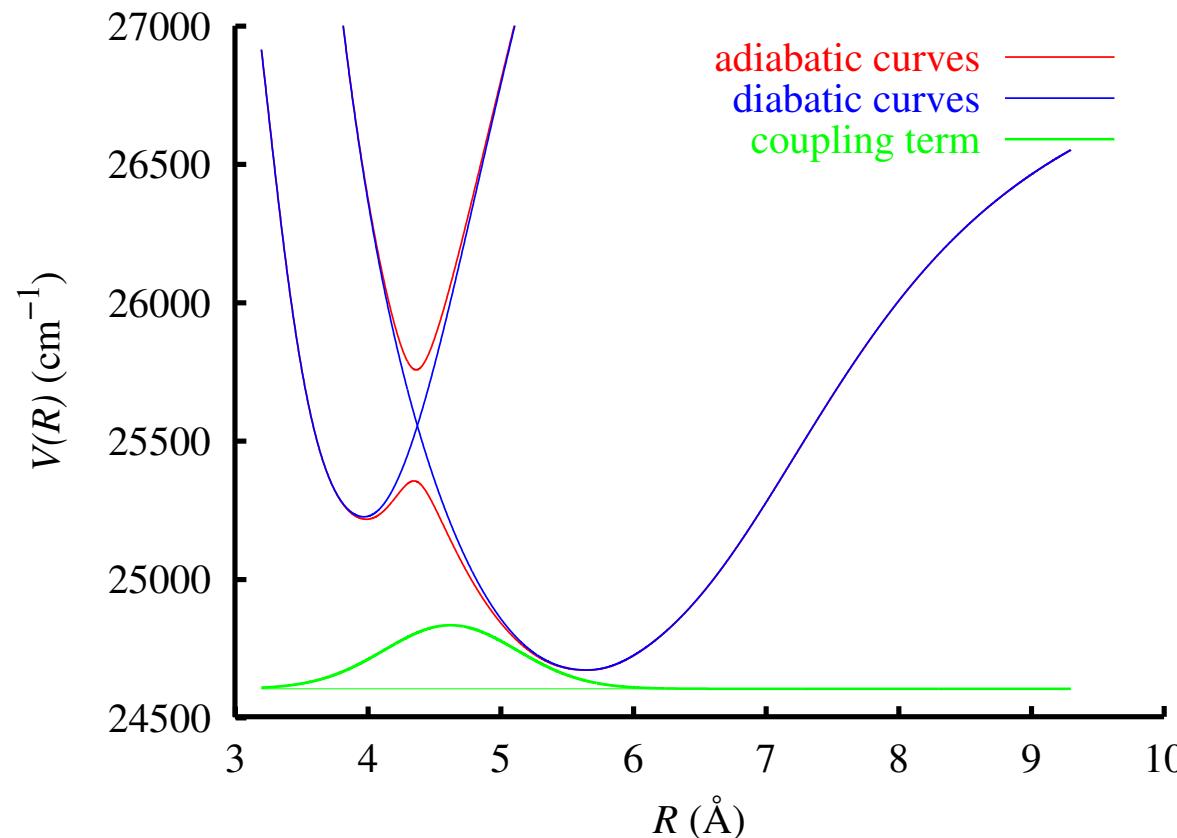


# DMM Fit for $3^3\Pi$ and $4^3\Pi$ States

The diabatic mixing model (DMM) fit:

- an analytic diabatic Hamiltonian
- non-linear least squares fit
- Results:

rms deviation  
for ro-vib. levels:  
 $0.24\text{cm}^{-1}$

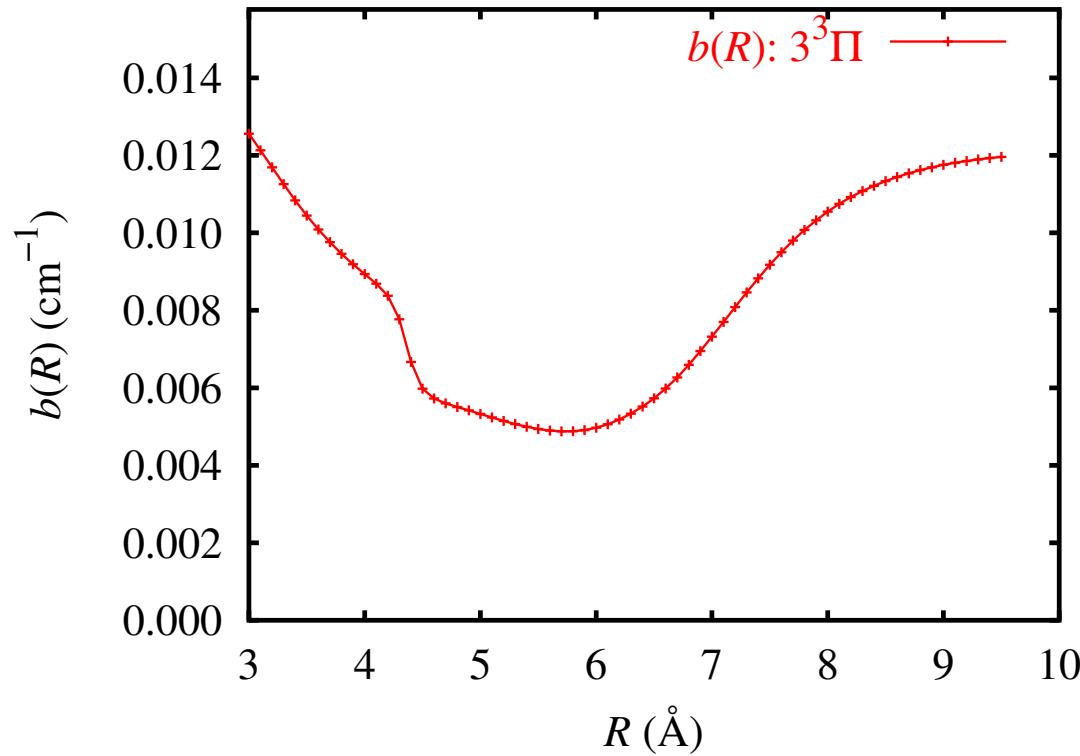


# Calculating $b(R)$ :

$$b(R) = \frac{4\pi\alpha^2}{3I} \frac{m}{M} E_h g_{\text{Na}} \rho_{\text{spin}}(R) a_0^3.$$

- Performed UHF calculations using the GAMESS electronic structure code developed at Iowa State University.
- Calculated diabatic potential curves and a separate  $b(R)$  for each diabatic state.
- For the  $3^3\Pi$  state, we take the appropriate weighted average at each  $R$ .

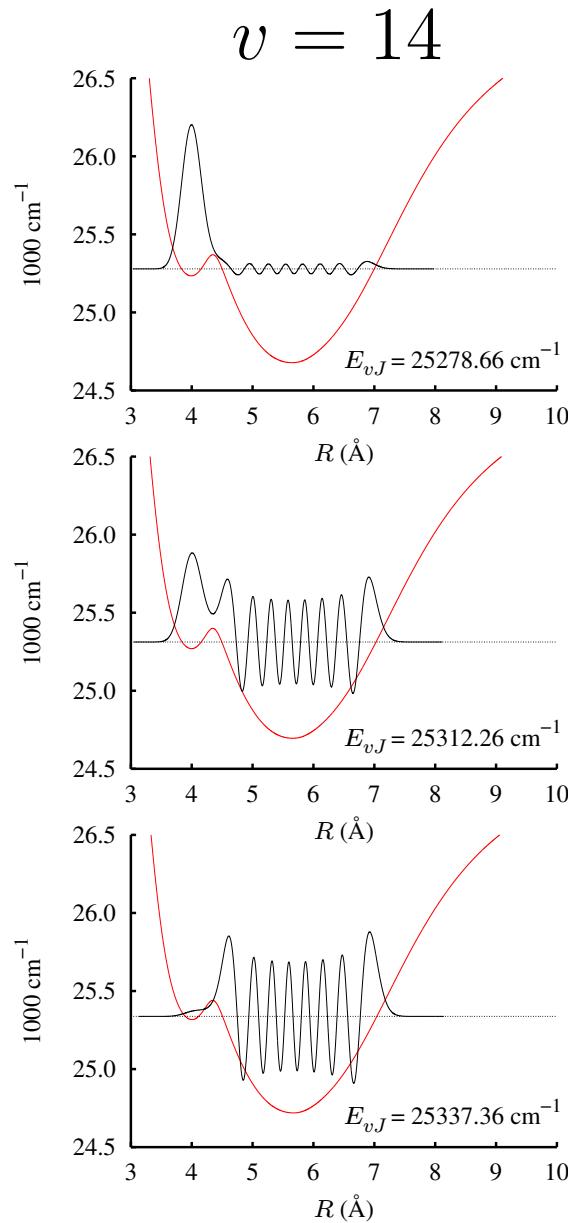
# $b(R)$ for $3^3\Pi$



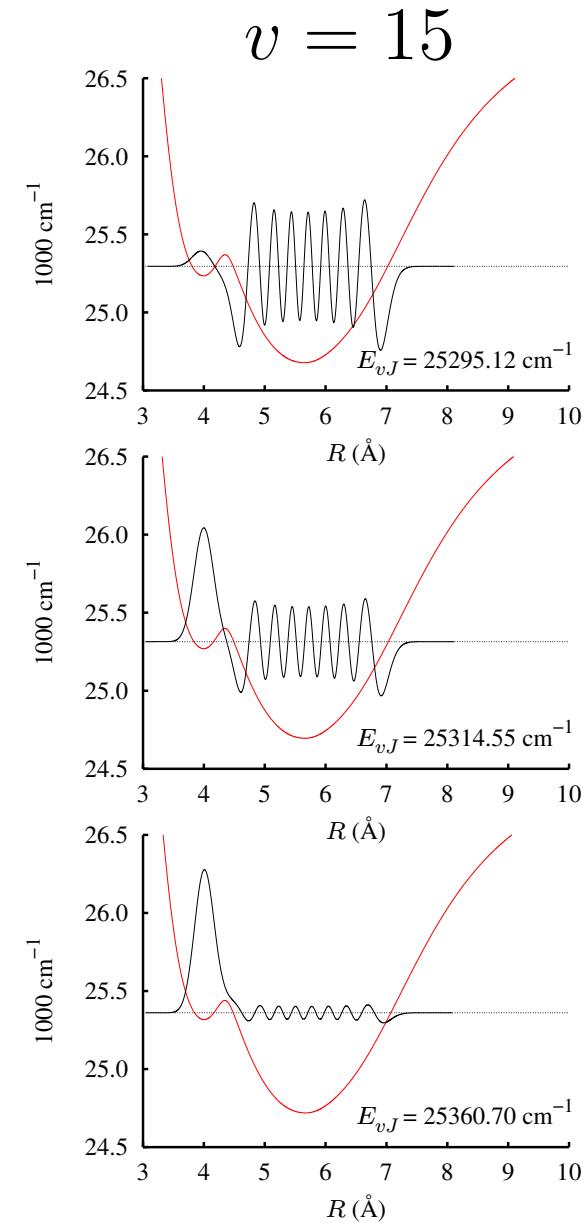
Transform dependence on  $R$  to  $v$ :

$$b_{vJ} = \int |\psi_{vJ}(R)|^2 b(R) dR$$

# Vibrational Wave Functions



$J = 16$

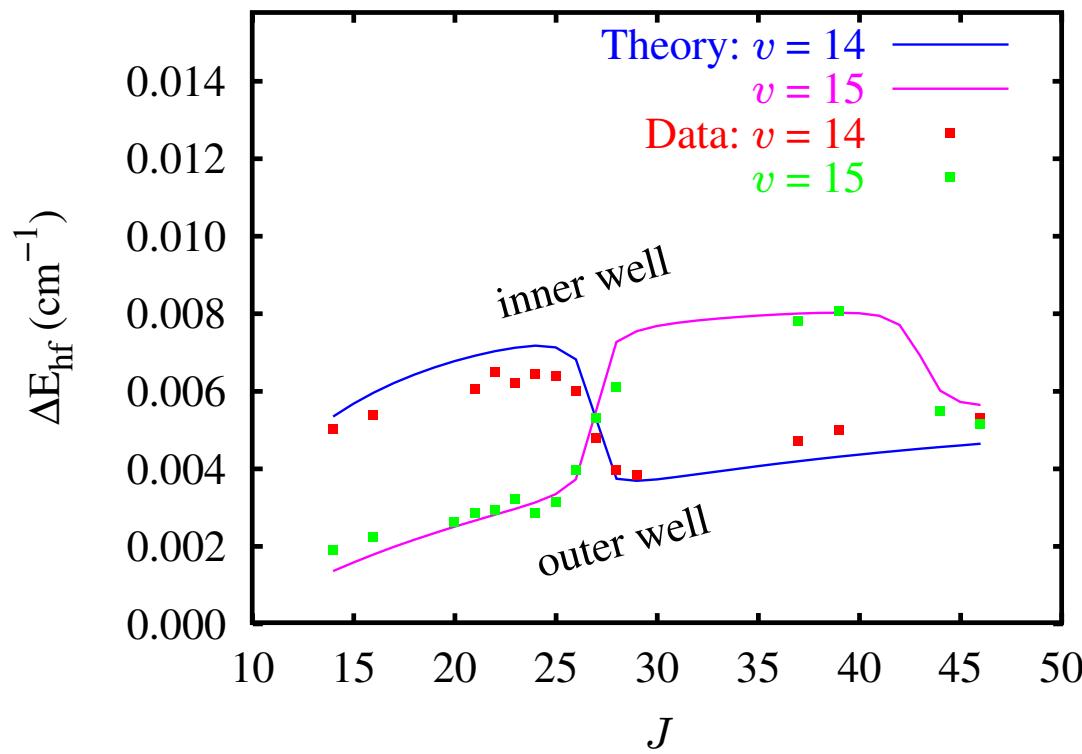


$J = 27$

$J = 37$

# Theoretical Hyperfine for $3^3\Pi$

We use the calculated values of  $b$  for each  $v, J$  level to set up a  $12 \times 12$  Hamiltonian matrix, which is diagonalized to find the hyperfine energy levels.



# Conclusions

- A double well state can be accurately fit to an analytic diabatic Hamiltonian.
- The hyperfine structure can be used as a probe to gain valuable information about the electronic structure of the molecule.

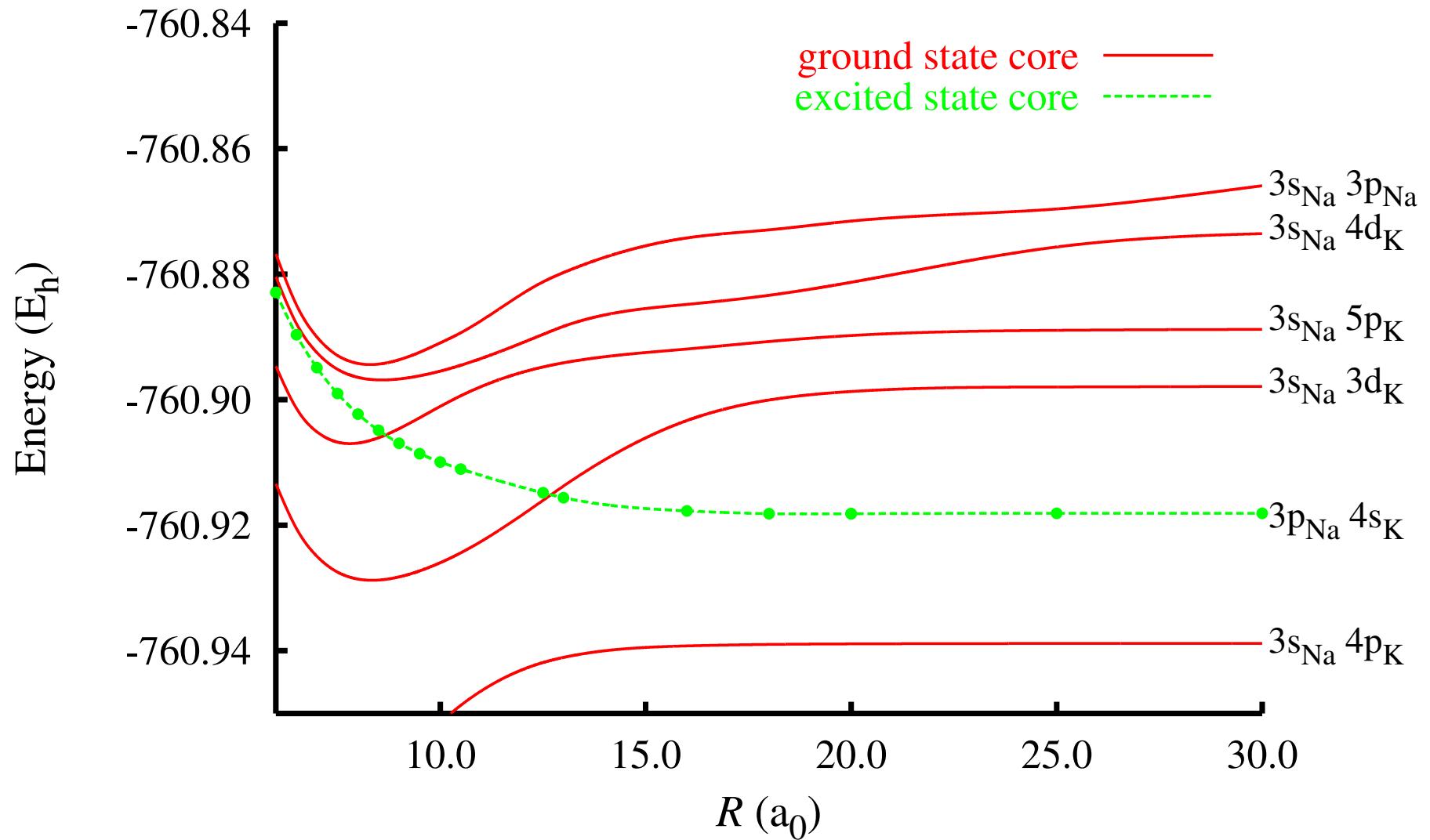
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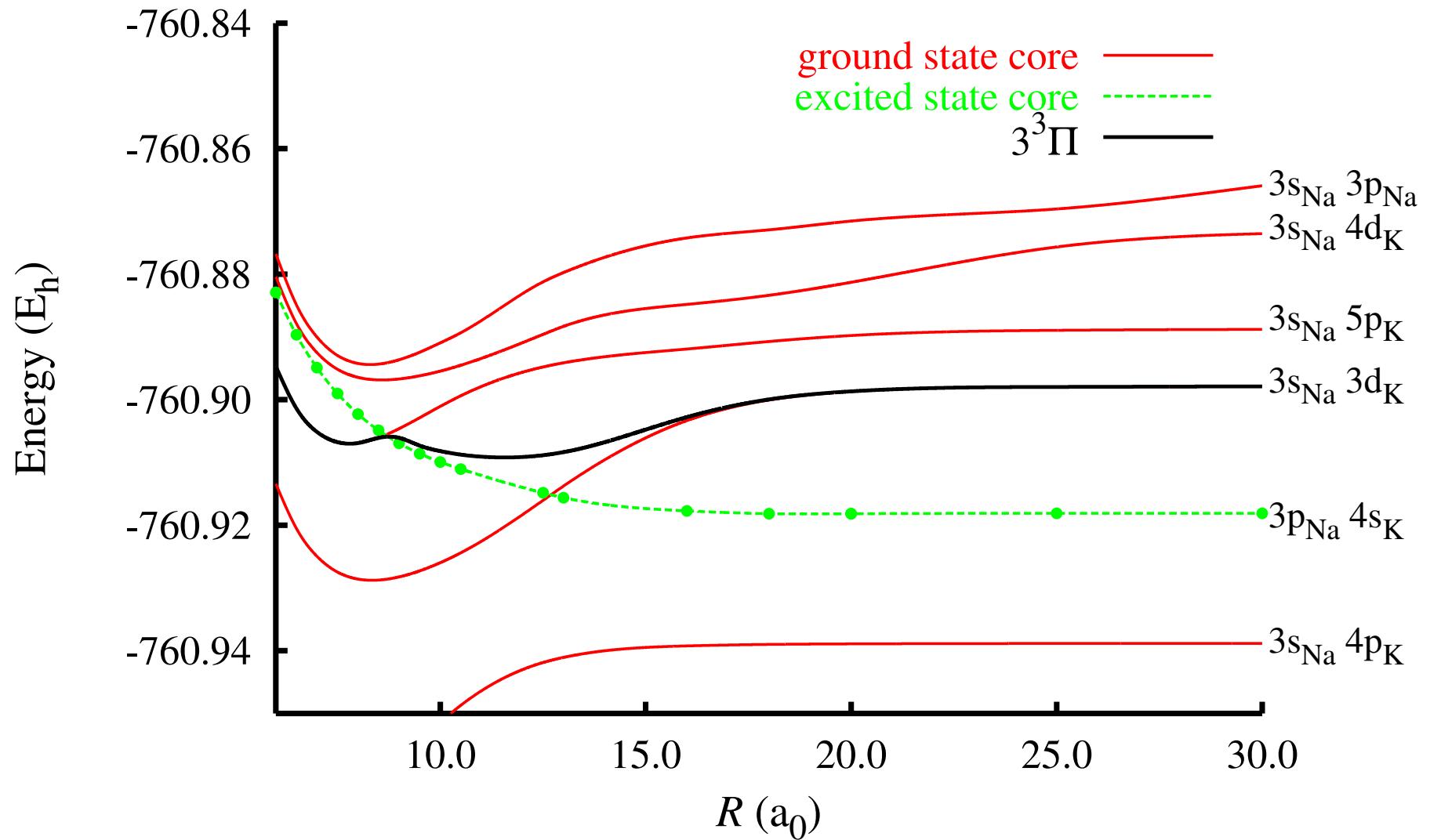
# *ab initio* Calculations

- GAMESS electronic structure calculations
  - MCSCF (Multi Configurational Self Consistent Field)
  - CI (Configuration Interaction)
  - UHF (Unrestricted Hartree Fock, for spin density of NaK<sup>+</sup>)
- 29s21p8d/16s12p8d basis: TZV basis, augmented by long range functions.
- block diagonalization method is used to get diabatic curves.

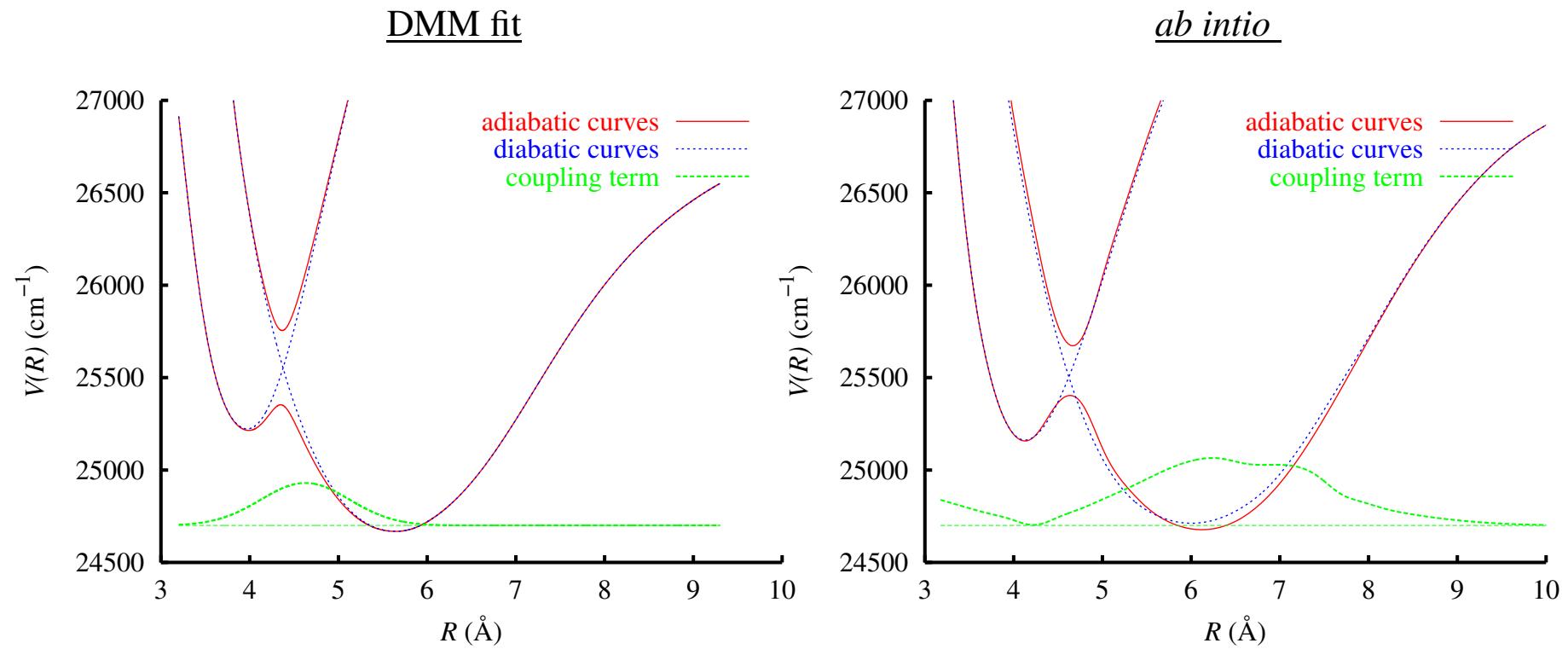
# *ab initio* diabatic potential curves



# *ab initio* diabatic potential curves



# Comparing *ab initio* to DMM fit



# Equation for $b(R)$ <sup>1</sup>

$$b(R) = \frac{4\pi\alpha^2}{3I} \frac{m}{M} E_h g_{\text{Na}} \rho(R) a_0^3.$$

Where  $\rho(R) = \rho_{\text{spin}\uparrow}(R) - \rho_{\text{spin}\downarrow}(R)$ .

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Our model is that  $b(R)$  is determined by the ion core part of the electronic wave function.

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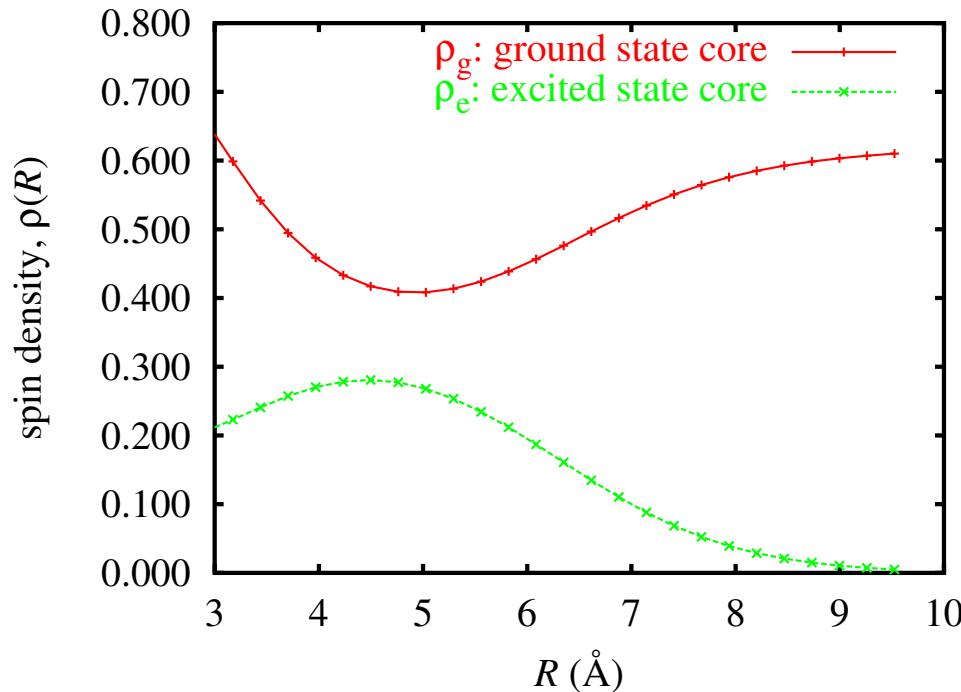
$$b(R) = \frac{4\pi\alpha^2}{3I} \frac{m}{M} E_h g_{\text{Na}} \rho(R) a_0^3.$$

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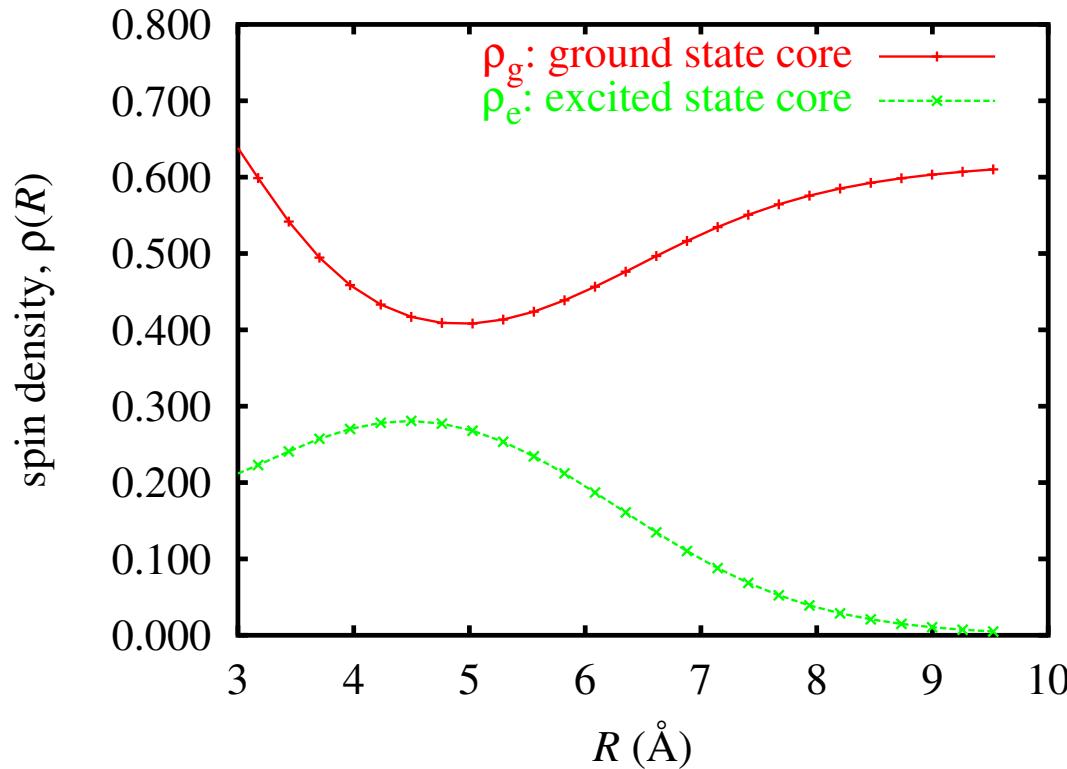
The ion core part of the adiabatic wave function can be determined from the diabatic Hamiltonian.

# $\rho(R)$ for NaK<sup>+</sup>



- Spin density at the Na nucleus of NaK<sup>+</sup>, from UHF calculations for ground and first excited state.

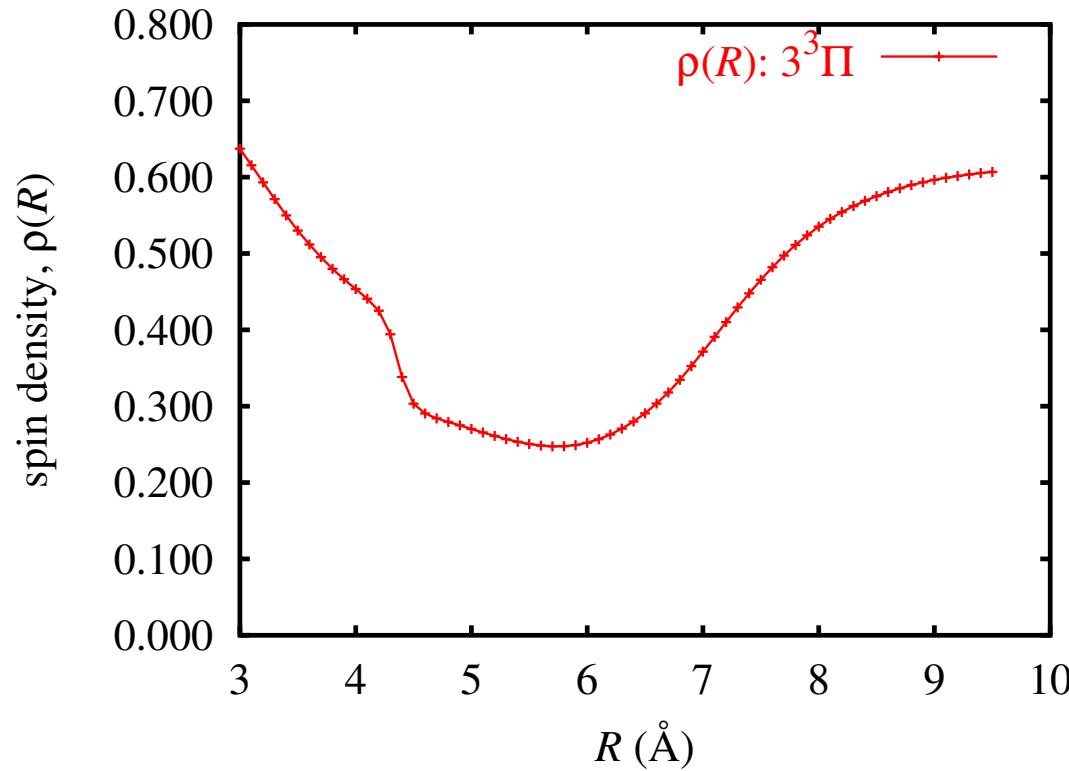
# $\rho(R)$ for $3^3\Pi$



The weighted average:

$$\rho(R) = P_g(R) \rho_g(R) + P_e(R) \rho_e(R).$$

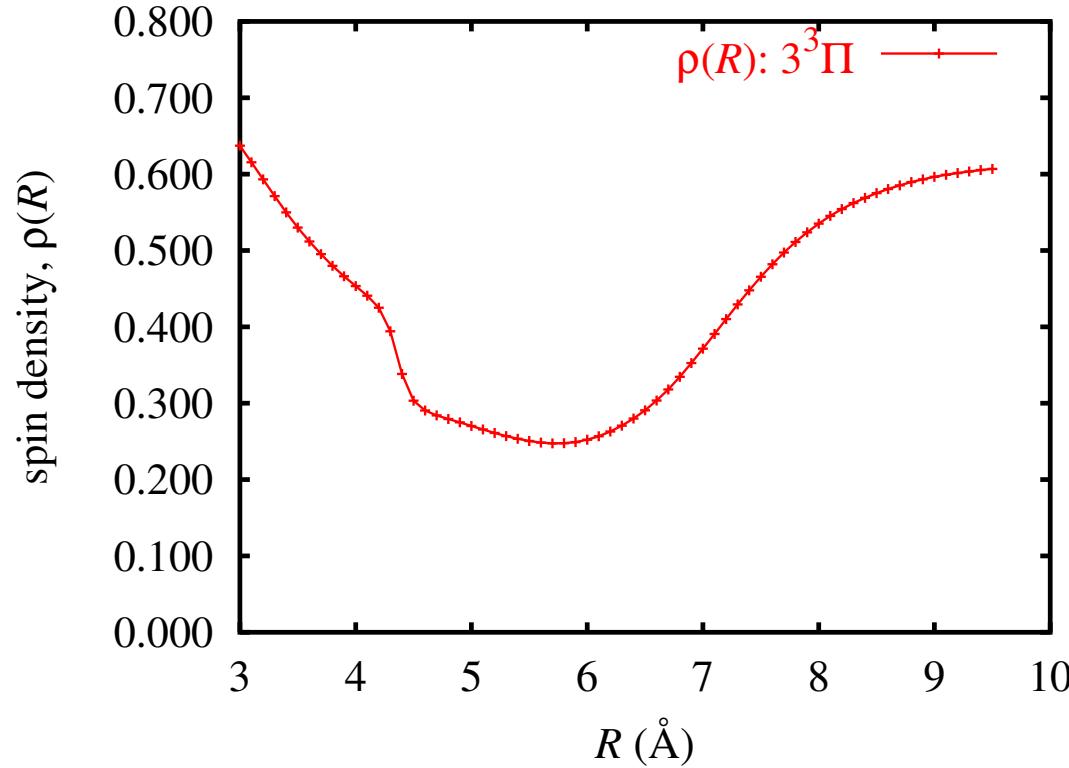
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The weighted average:

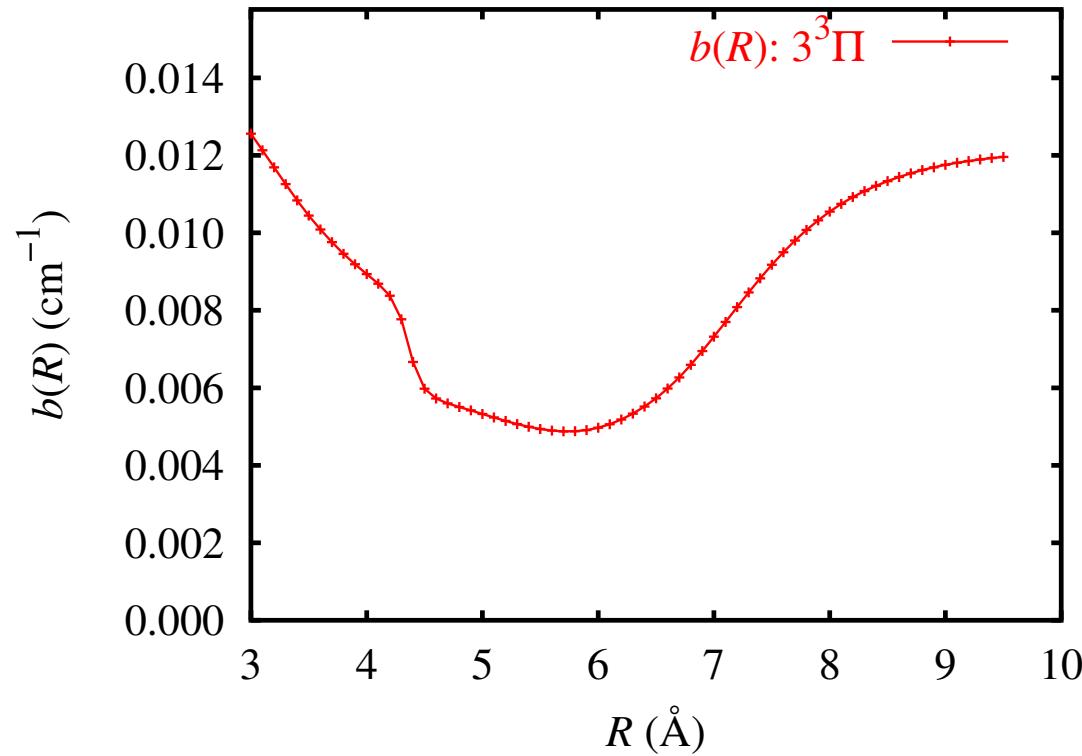
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# $\rho(R)$ for $3^3\Pi$



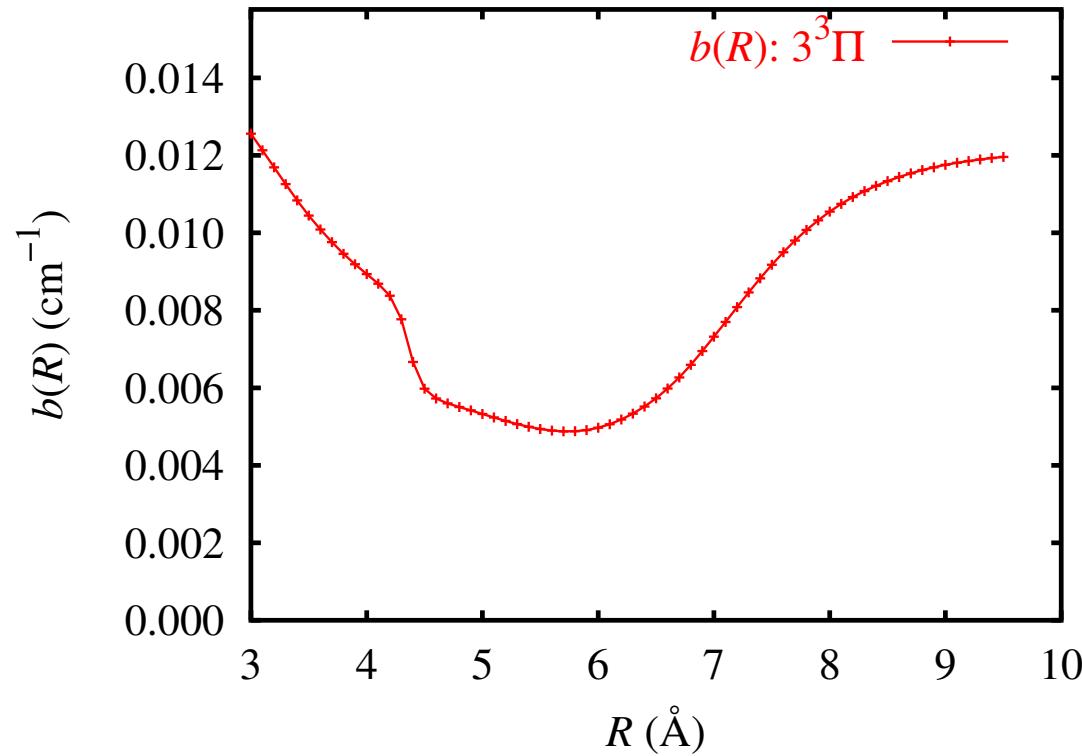
Multiply by  $(\frac{4\pi\alpha^2}{3I} \frac{m}{M} E_h g_{\text{Na}} a_0^3)$  to get  $b(R)$ .

# $b(R)$ for $3^3\Pi$



Multiply by  $(\frac{4\pi\alpha^2}{3I} \frac{m}{M} E_{\text{h}} g_{\text{Na}} a_0^3)$  to get  $b(R)$ .

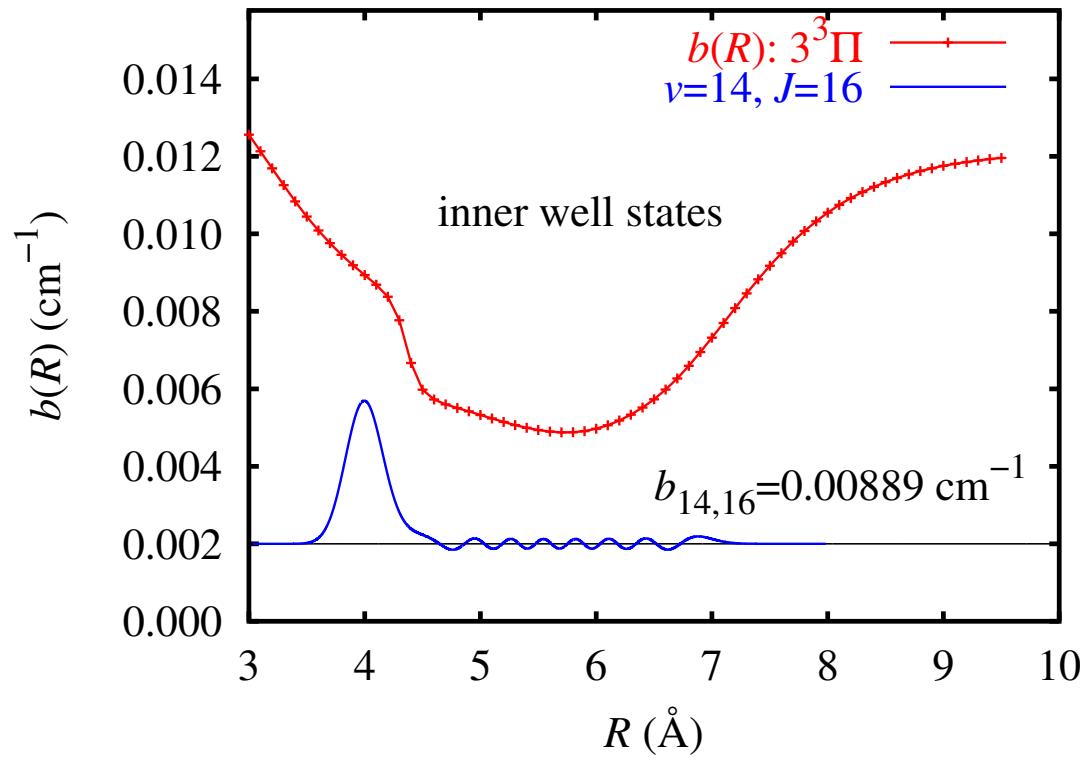
# $b(R)$ for $3^3\Pi$



Then, transform dependence on  $R$  to  $v$ :

$$b_{vJ} = \int |\psi_{vJ}(R)|^2 b(R) dR$$

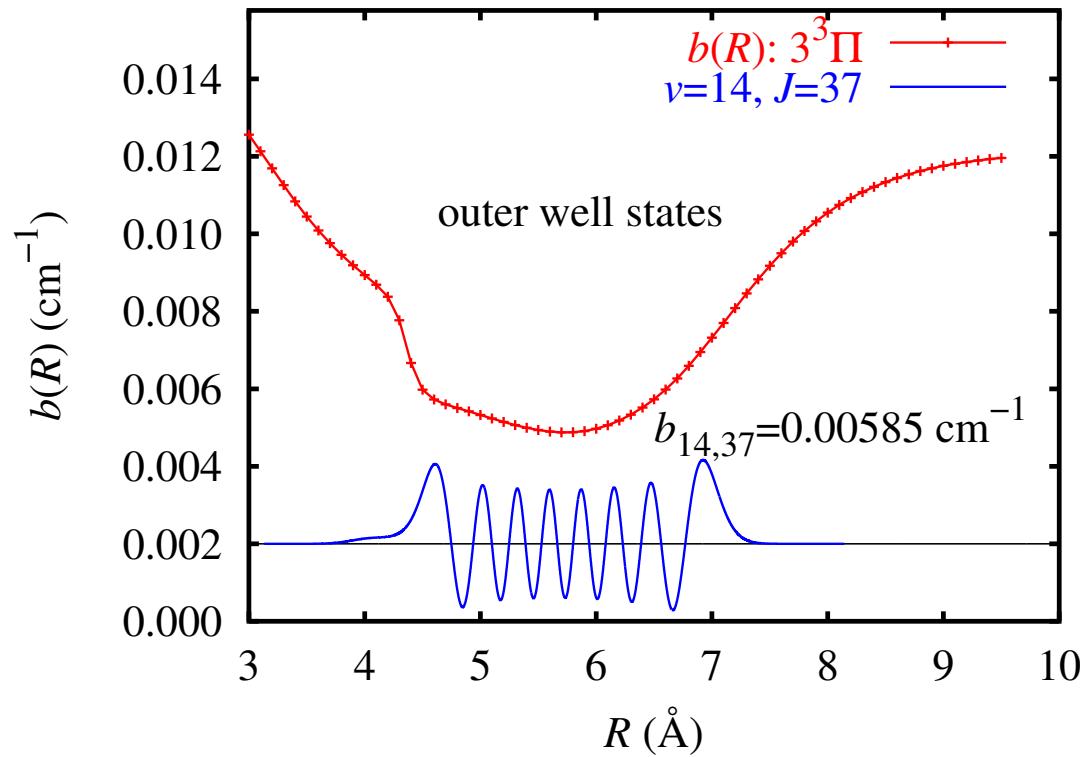
# $b_{vJ}(R)$ for $3^3\Pi$



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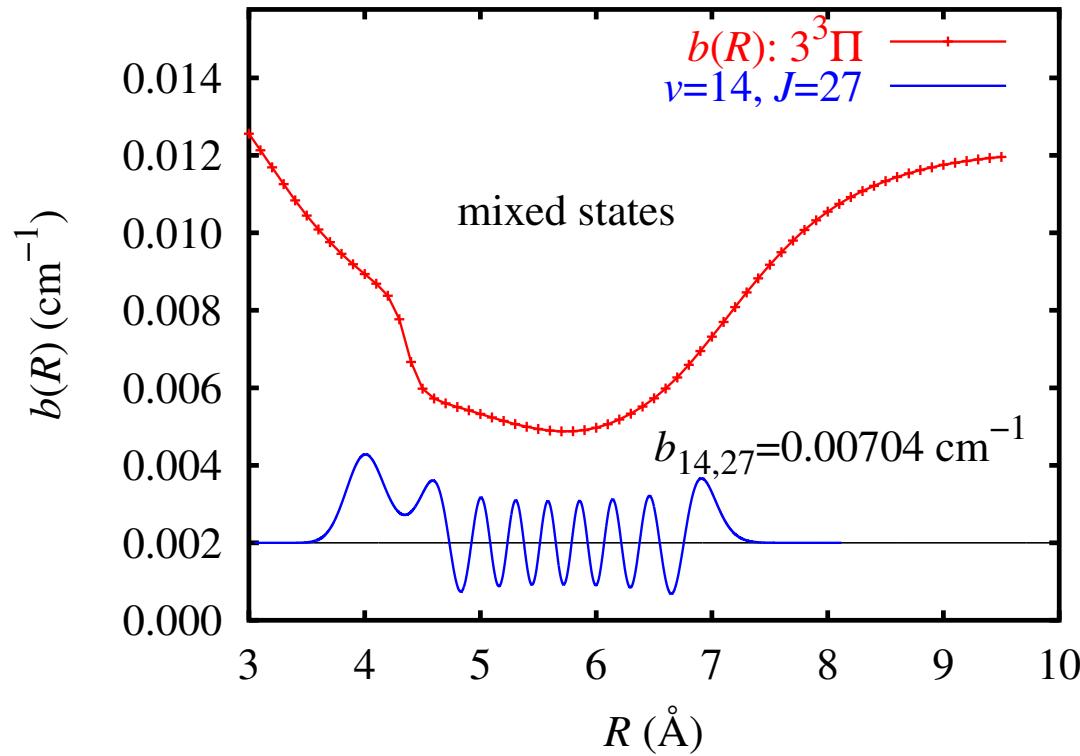
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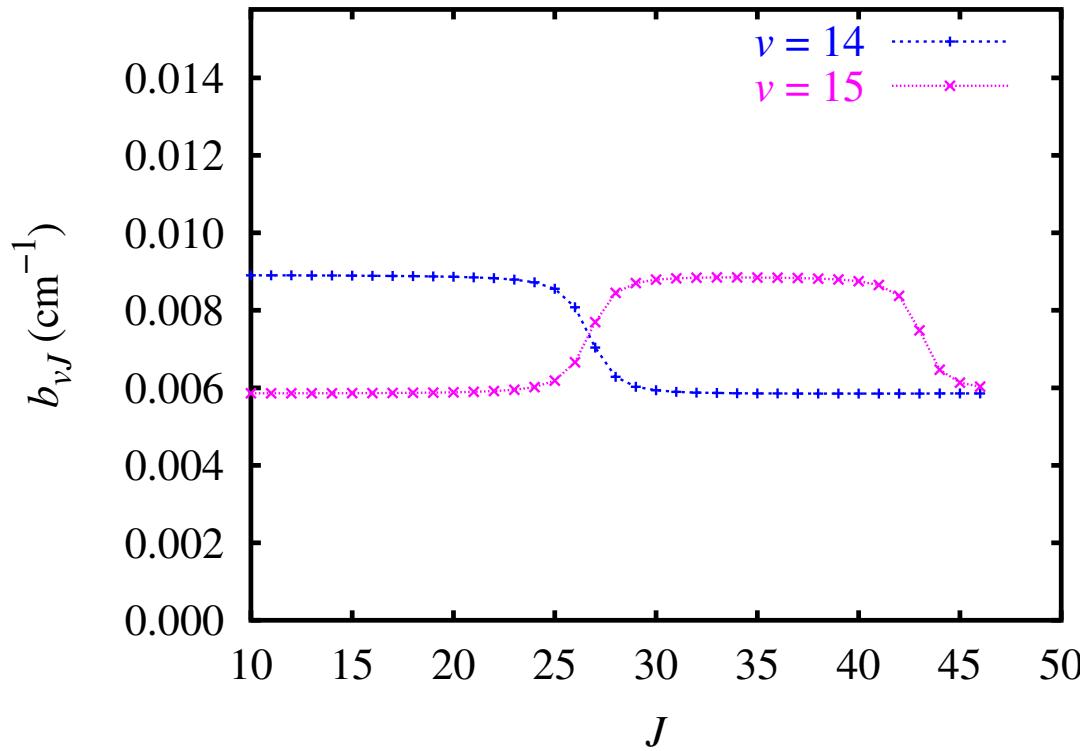
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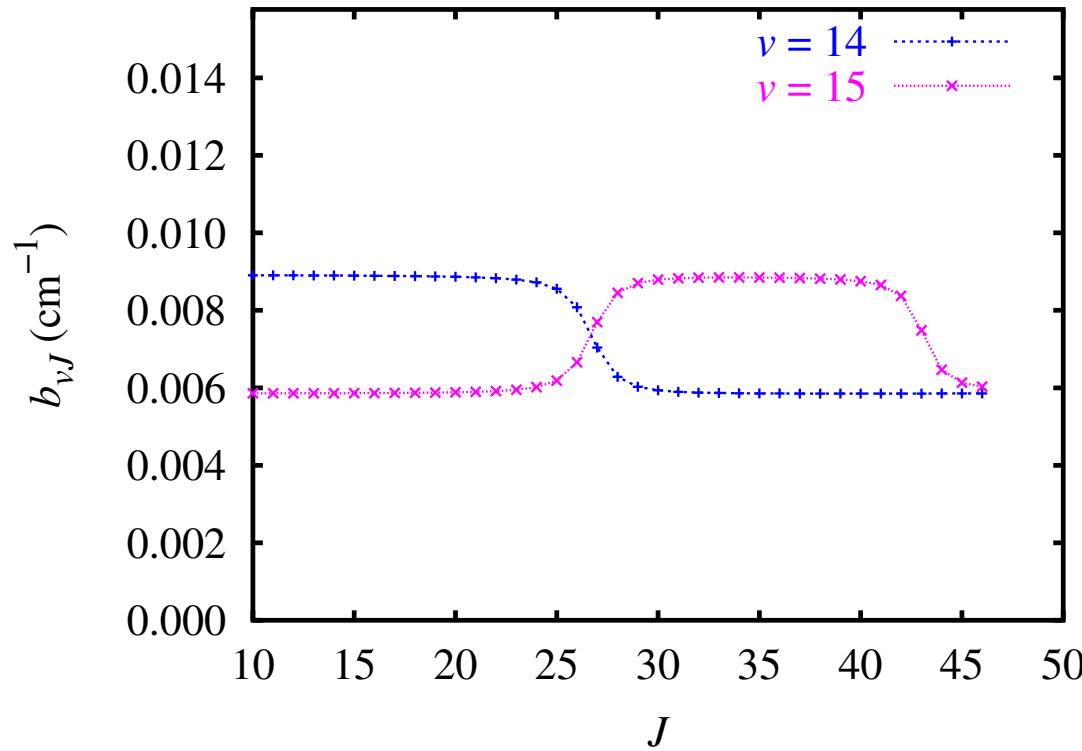
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Then, transform dependence on  $R$  to  $v$ :

$$b_{vJ} = \int |\psi_{vJ}(R)|^2 b(R) dR$$

# $b_{vJ}$ for $3^3\Pi$



Finally, we calculate the hyperfine structure using this calculation of  $b_{vJ}$ .

# Hyperfine Structure Calculation

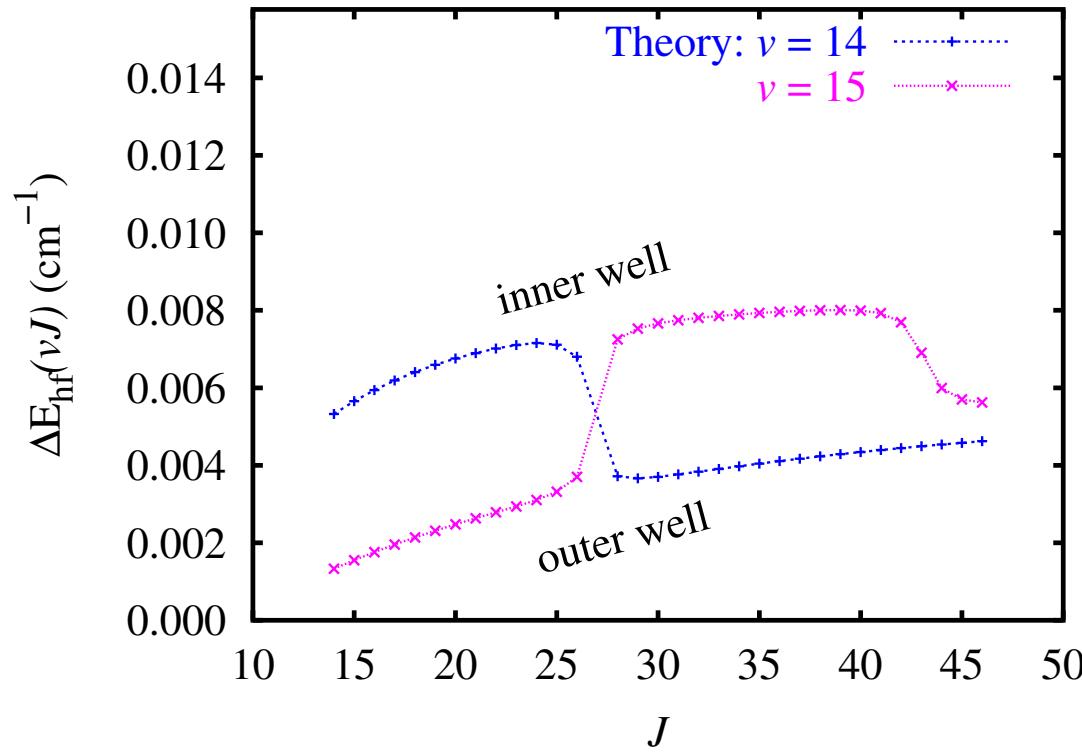
These are the important terms in our model Hamiltonian:

$$\mathbf{H} = \mathbf{H}_{\text{rotation}} + \mathbf{H}_{\text{spin-orbit}} + \mathbf{H}_{\text{hyperfine}}$$

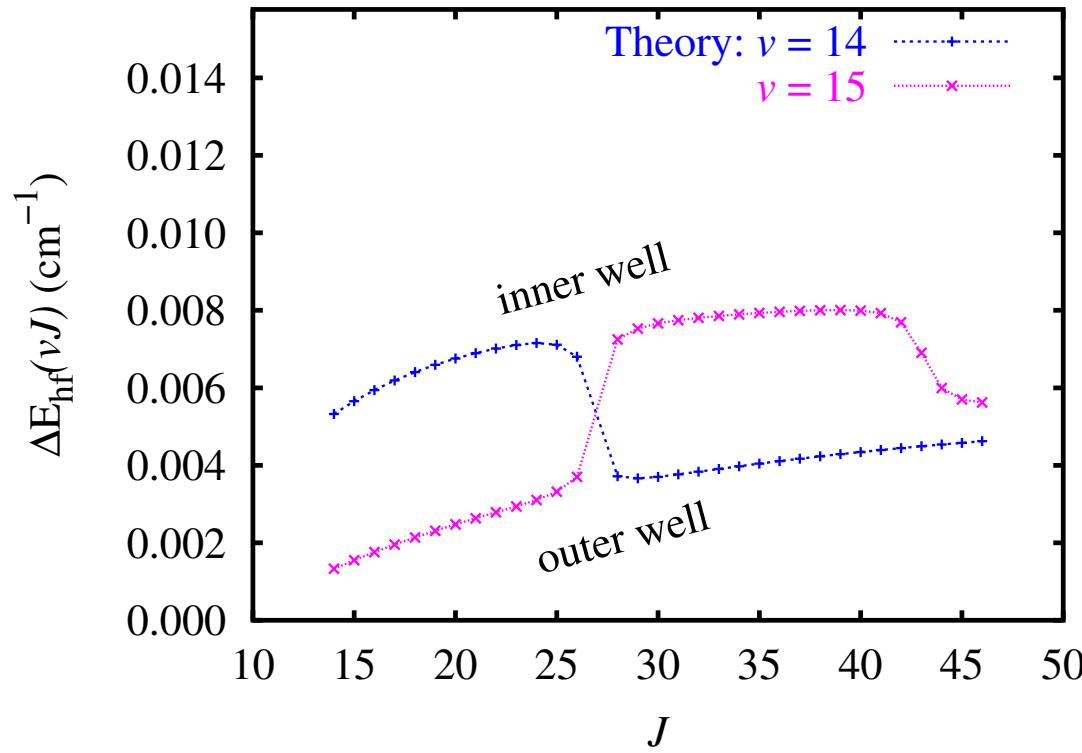
$$\mathbf{H} = B\mathbf{N}(\mathbf{N} + 1) + A\mathbf{L} \cdot \mathbf{S} + b_{vJ}\mathbf{I} \cdot \mathbf{S}$$

Using this Hamiltonian, we form a  $12 \times 12$  Hamiltonian and diagonalize to find the eigenstates of the system.

# Theoretical Hyperfine for $3^3\Pi$



# Theoretical Hyperfine for $3^3\Pi$



Compare to experimental data.