

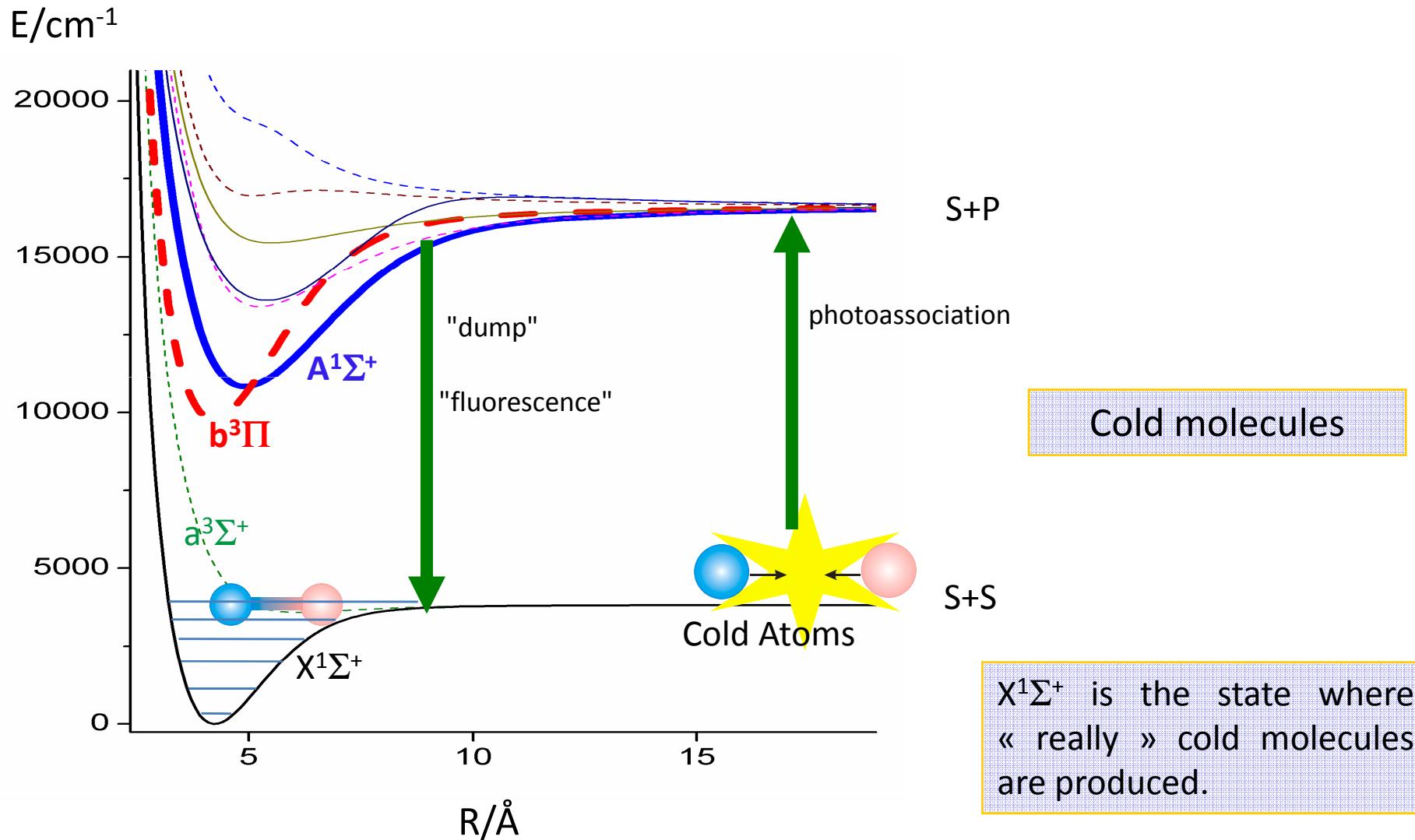


# Study of the A<sup>1</sup>Σ<sub>u</sub><sup>+</sup> and b<sup>3</sup>Π<sub>0u</sub> states in Cs<sub>2</sub>: New data and global analysis

Houssam Salami, Tom Bergeman, Olivier Dulieu,

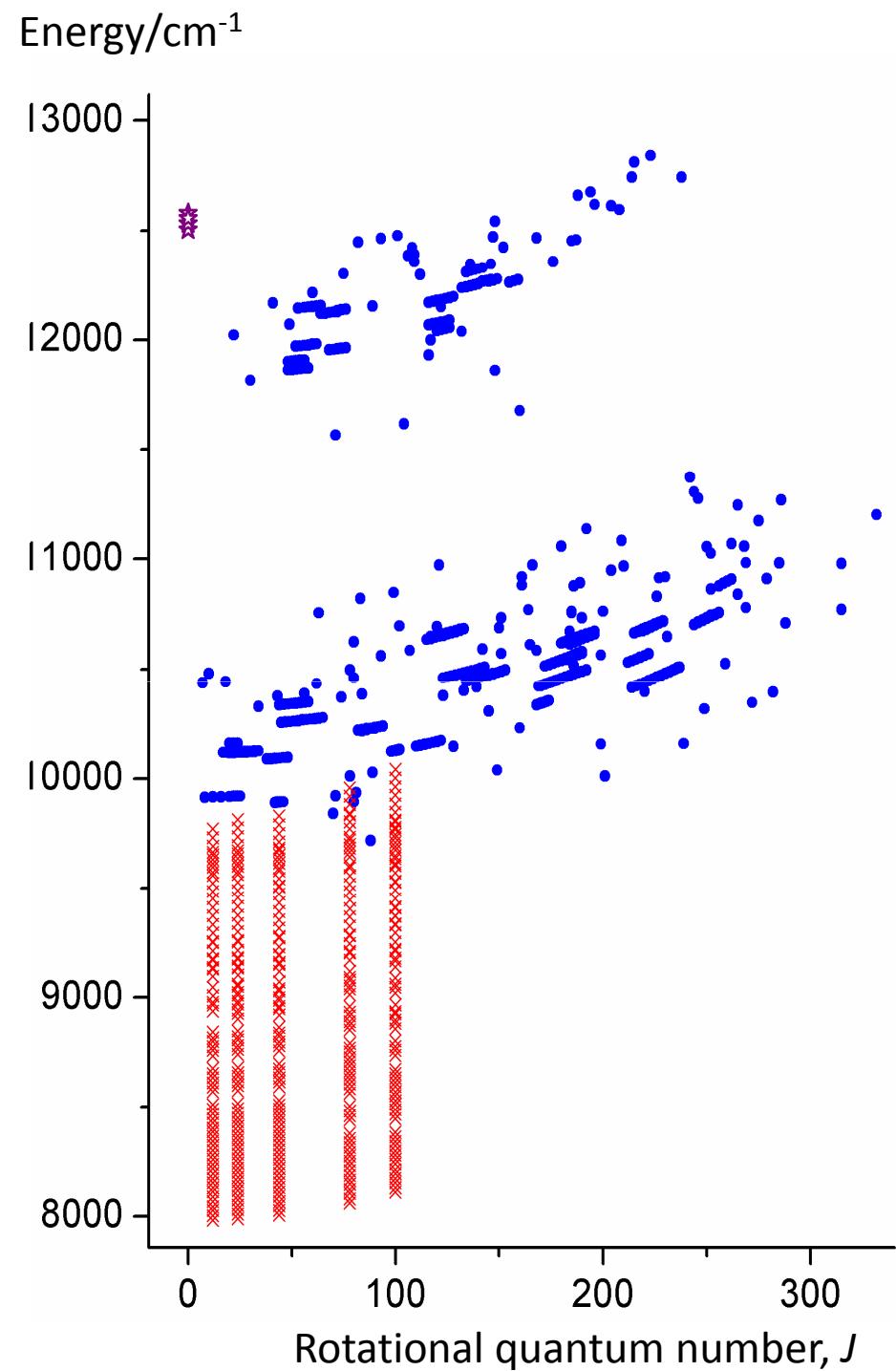
Dan Li, Feng Xie and LiLi

# Description of the $A^1\Sigma_u^+$ and $b^3\Pi_{0u}$ states correlated to the atomic asymptote $Cs(6s)+Cs(6p)$



# $\text{Cs}_2$ , $\text{A}^1\Sigma^+$ and $b^3\Pi_{0u}$ data

- Fourier Transform Spectroscopy (FTS) data from the Laboratoire Aimé Cotton website, from the work of Claude Amiot and Olivier Dulieu, J. Chem. Phys. 117, 5155 (2002).
- ✖ Fluorescence spectroscopy data from Tsinghua University, from the work of Feng Xie, Dan Li, Luke Tyree, Li Li, Vladimir Sovkov, Valery Ivanov, Sylvie Magnier and A. Marjatta Lyyra, recently submitted to J. Chem. Phys
- ★ Very recent measurements of excitation from Feshbach resonance states by J. Danzl and H. C. Nägerl at Innsbruck



# The DVR Method\*

- DVR method computes perturbed wavefunctions to a high degree of accuracy, because all mesh points are used to obtain  $d^2/dR^2$
- Kinetic Energy is represented by a full matrix over the mesh points,

$$T_{ii'} = \frac{\hbar^2 (-1)^{i-i'}}{2m\Delta R^2} \begin{cases} \frac{\pi^2/3}{2} & i = i' \\ \frac{2}{i - i'} & i \neq i' \end{cases} \quad R_i = i\Delta R$$

- The potential energies are diagonal,  $V_{ii'} = \delta_{ii'} (R_i)$
- Hamiltonian matrix,  $n \times n$   
 $n = \text{number of R mesh points} \times \text{number of channels}$  ( ${}^1\Sigma_u^+$ ,  ${}^3\Pi_{0u}$ , etc).

\* Colbert and Miller, Journal of Chemical Physics **96**, 1982 (1992)

# Coupled Channel Analysis

Hamiltonian matrix:

$$\begin{matrix}
 & A^1\Sigma_u^+ & b^1\Pi_{0u} \\
 A^1\Sigma_u^+ & V\left(^1\Sigma_u^+\right) + (x+2)B & -\Delta_{od} \\
 b^1\Pi_{0u} & -\Delta_{od} & V\left(^1\Pi_u\right) - \Delta_d + (x+2)B
 \end{matrix}$$

Spin-orbit functions:

$$y_{s.o.} = p_1 + (p_2 - p_1) \left[ 1 - e^{p_3(p_4 - R)} \right]$$

Atomic  
fine structure  
interval

$$\begin{aligned}
 p_1 &= y_{s.o.}(R_m) \\
 p_2 &= y_{s.o.}(\infty) = \sqrt{2}\Delta/3 \\
 p_4 &= R_m
 \end{aligned}$$

Hannover

Potential:

$$V(R) = T_e + \sum_{i=2}^I a_i \left( \frac{R - R_e}{R + bR_e} \right)^i$$

or: Morse/long-range



## Modified Morse Potential/Long-Range (MLR)

$$V_{MLR}(R) = \mathcal{D}_e \left\{ 1 - \frac{\mathcal{U}_{LR}(R)}{\mathcal{U}_{LR}(R_e)} e^{-\phi_{MLR}(R)y_p(R)} \right\}^2 *$$

$$\mathcal{U}_{LR} = \frac{C_n}{R^n} + \frac{C_m}{R^m}$$

With theoretically predicted form at Long Range

$$V(R) = \mathcal{D}_e - C_n/R^n - C_m/R^m$$

### Dispersion coefficients:

$$C_3(A) = 6.8 \times 10^5 \text{ cm}^{-1}\text{\AA}^3, C_3(b) = 3.4 \times 10^5 \text{ cm}^{-1}\text{\AA}^3 \quad \text{Derevianko, Babb, Dalgarno, PRA 63, (2001) 052704}$$

$$C_6(A) = 8.4 \times 10^7 \text{ cm}^{-1}\text{\AA}^6, C_6(b) = 8.4 \times 10^7 \text{ cm}^{-1}\text{\AA}^6 \quad \text{Porsev, Derevianko, J. Chem. Phys. 119 (2003) 844}$$

---

**Dissociation energy:**  $\mathcal{D}_e(A) = 5283 \text{ cm}^{-1}, R_e(A) = 5.316 \text{ \AA}; \mathcal{D}_e(b) = 6404 \text{ cm}^{-1}, R_e(b) = 4.384 \text{ \AA}$

\* Published model: R. Le Roy, D. Henderson, Mol. Phys. 105, 663, 2007

## OTHER VARIABLES ?

$$V_{MLR}(R) = D_e \left\{ 1 - \frac{\mathcal{U}_{LR}(R)}{\mathcal{U}_{LR}(R_e)} e^{-\phi_{MLR}(R)y_p(R)} \right\}^2$$

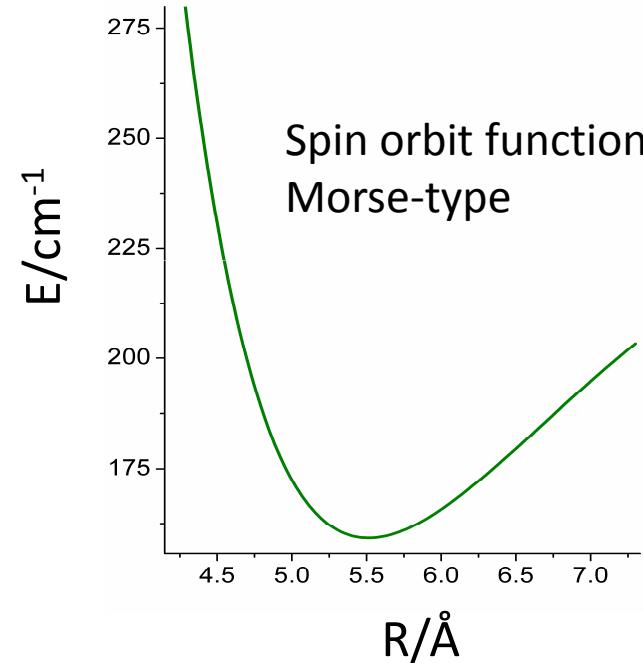
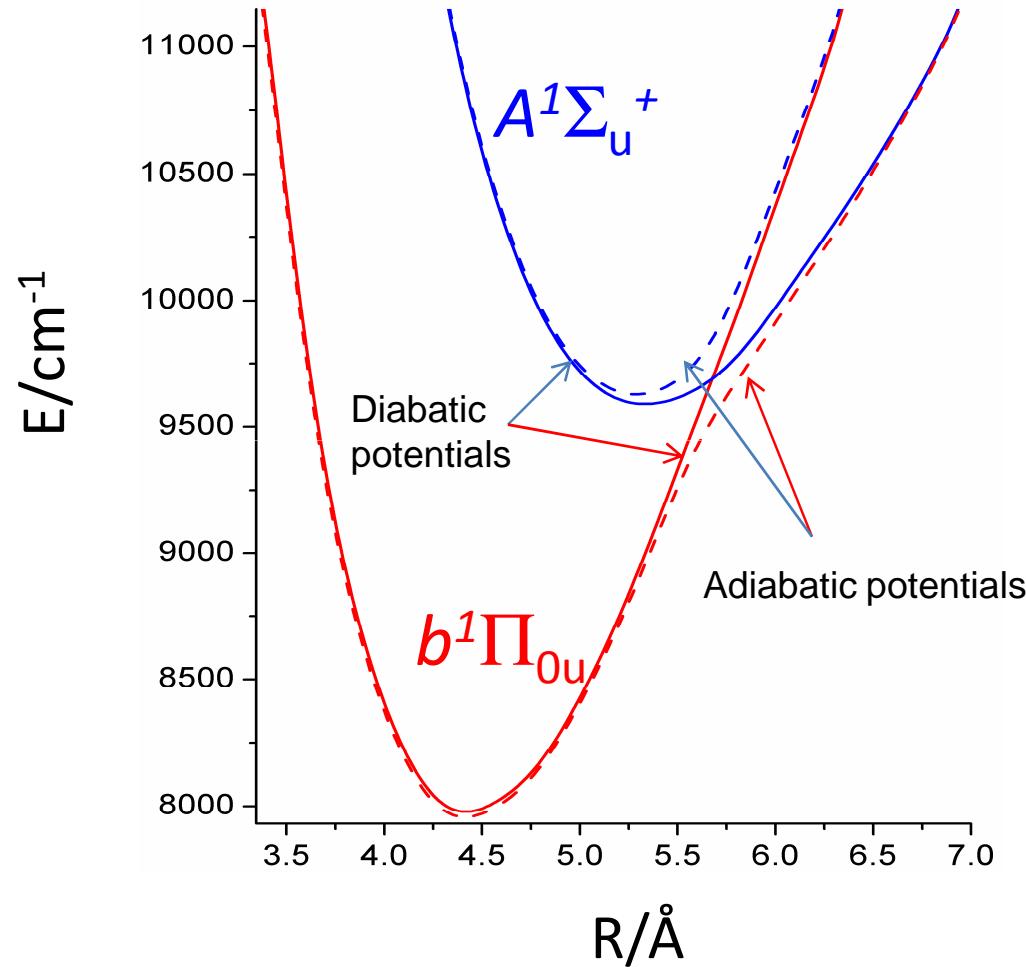
$$y_p(R) = \frac{(R^p - R_e^p)}{(R^p + R_e^p)} \quad p \text{ (integer)} > 3 \text{ imposed by } C_n \text{ constraints}$$

$$\phi_{MLR}(R) = \phi_\infty y_p(R) + [1 - y_p(R)] \sum_{i=0}^{N_{S(\text{or } L)}} \phi_i y_p(R)^i \quad \text{for } R \leq R_e \text{ or } (R > R_e)$$

with  $y_p \rightarrow 1$  when  $\underline{R \rightarrow \infty} \Rightarrow V(R) = D_e - C_n/R^n - C_m/R^m$

**OPTIMIZE  $N_S, N_L, p, \Phi_l$**

# Fitted MLR potentials and Morse SO function



Potential Energy Curves have been performed using DVR method

## Parameters in the MLR potential: $N_s$ , $N_L$ , $p$ , $\Phi$ and in S.O functions

	$A^1\Sigma_u^+$	$b^3\Pi_{0u}$
	$p=4, N_s=4, N_L=10$	$p=4, N_s=4, N_L=11$
$\Phi_1$	0.53324(11)D+01	0.44162(75)D+01
$\Phi_2$	0.5283(10)D+04	0.6404D+04*
$\Phi_3$	0.958854(21)D+04	0.797839(73)D+04
$\Phi_4$	-0.10229(37)D+01	-0.1238(15)D+01
$\Phi_5$	-0.1020(34)D+01	-0.1633(60)D+01
$\Phi_6$	-0.256(26)D+01	-0.1046(76)D+02
$\Phi_7$	-0.274(72)D+01	-0.273(26)D+02
$\Phi_8$	-0.959(677)D+00	-0.246(26)D+02
$\Phi_9$	0.8558(590)D+04	0.1903(52)D+05
$\Phi_{10}$	-0.865(56)D+05	-0.2014(36)D+06
$\Phi_{11}$	0.360(20)D+06	0.952(12)D+06
$\Phi_{12}$	-0.759(34)D+06	-0.2483(21)D+07
$\Phi_{13}$	0.8028204190232D+06	0.3701(21)D+07
$\Phi_{14}$	-0.3385607464000D+06	-0.29652(86)D+07
		0.992(26)D+06

$$V_{MLR}(R) = \mathcal{D}_e \left\{ 1 - \frac{\mathcal{U}_{LR}(R)}{\mathcal{U}_{LR}(R_e)} e^{-\phi_{MLR}(R) y_p(R)} \right\}^2$$

Spin-Orbit Function:

$$y_{s.o.} = p_1 + (p_2 - p_1) [1 - e^{p_3(p_4 - R)}]$$

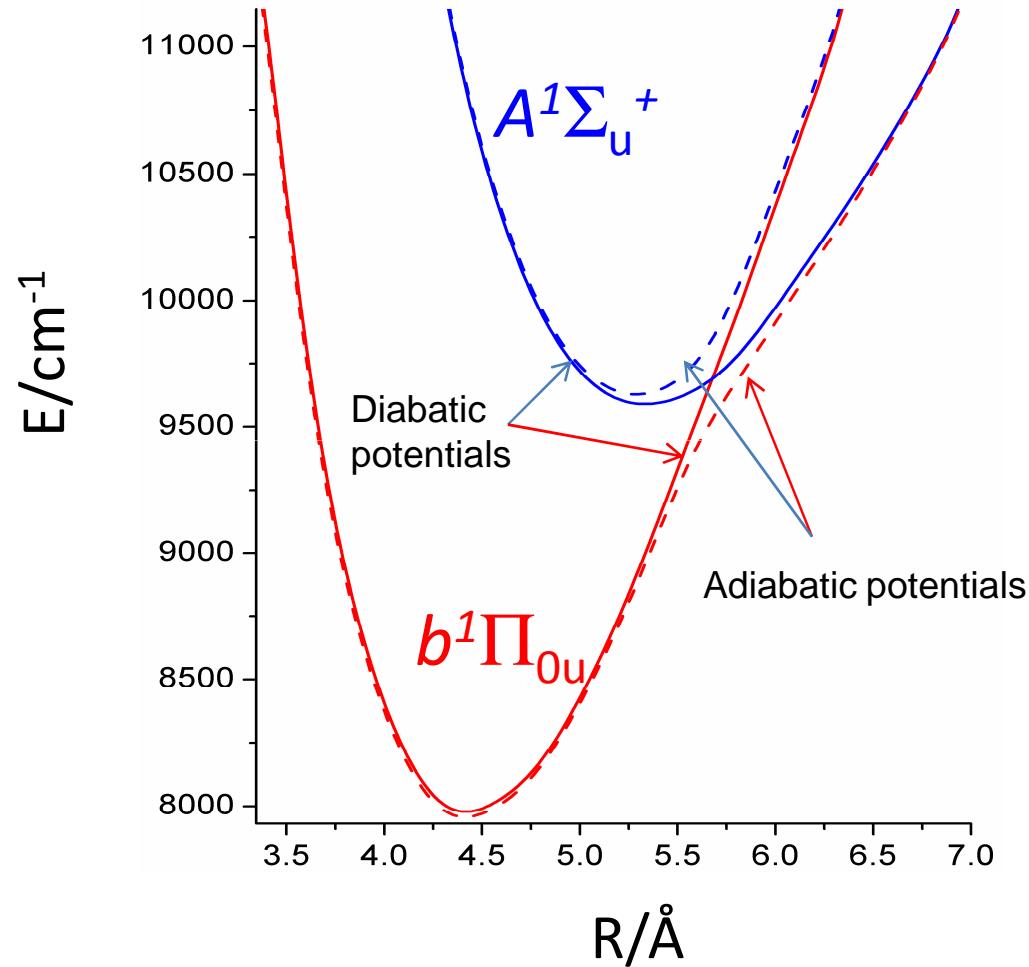
$$p_1 = y_{s.o.}(R_m) = 159.2(3)$$

$$p_2 = y_{s.o.}(\infty) = 261.2$$

$$p_3 = 0.600(5)$$

$$p_4 = R_m = 5.513(6)$$

# Fitted MLR potentials and Morse S.O. function

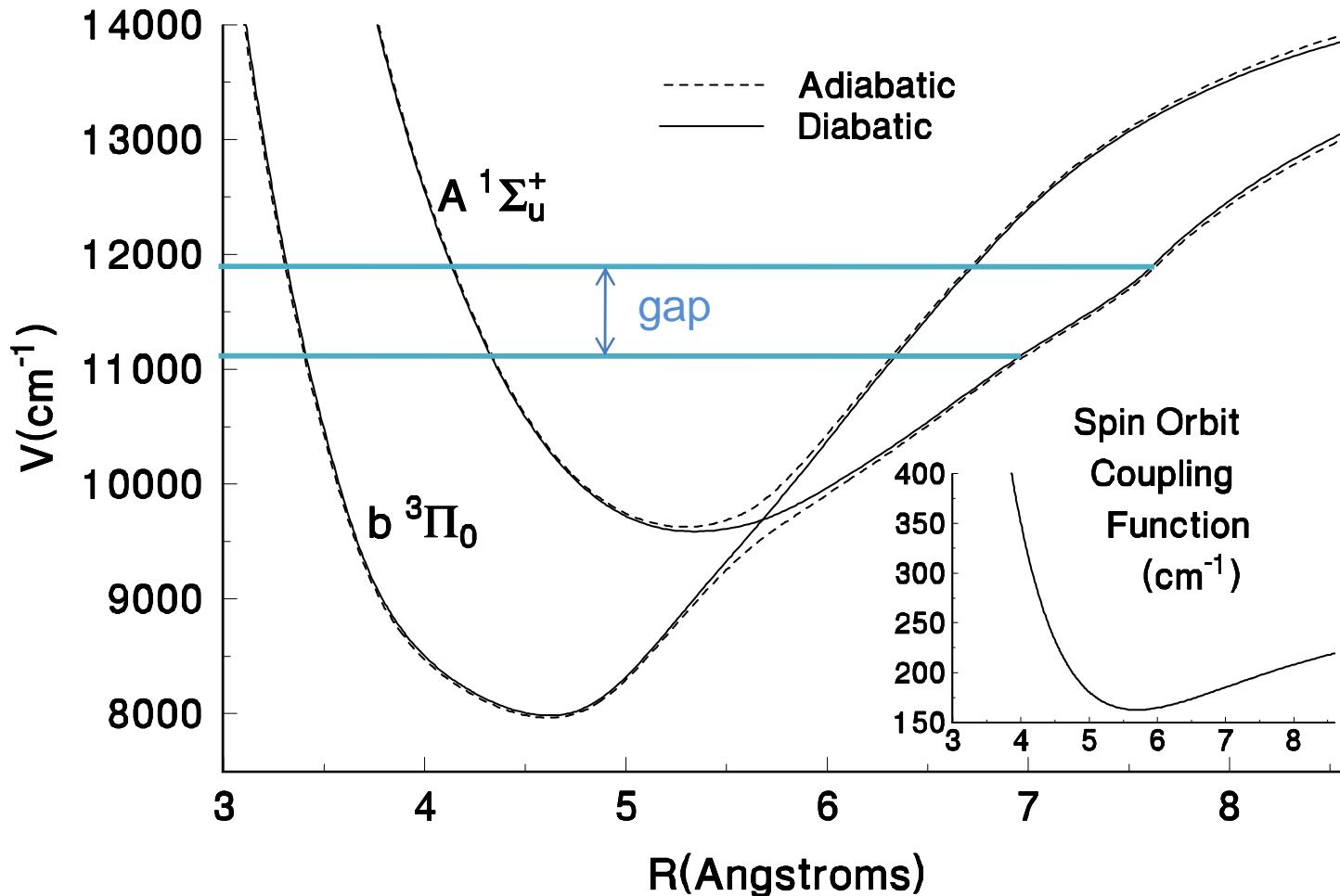


Rms deviation  
(using Morse/Long-Range)  
=  $0.07 \text{ cm}^{-1}$

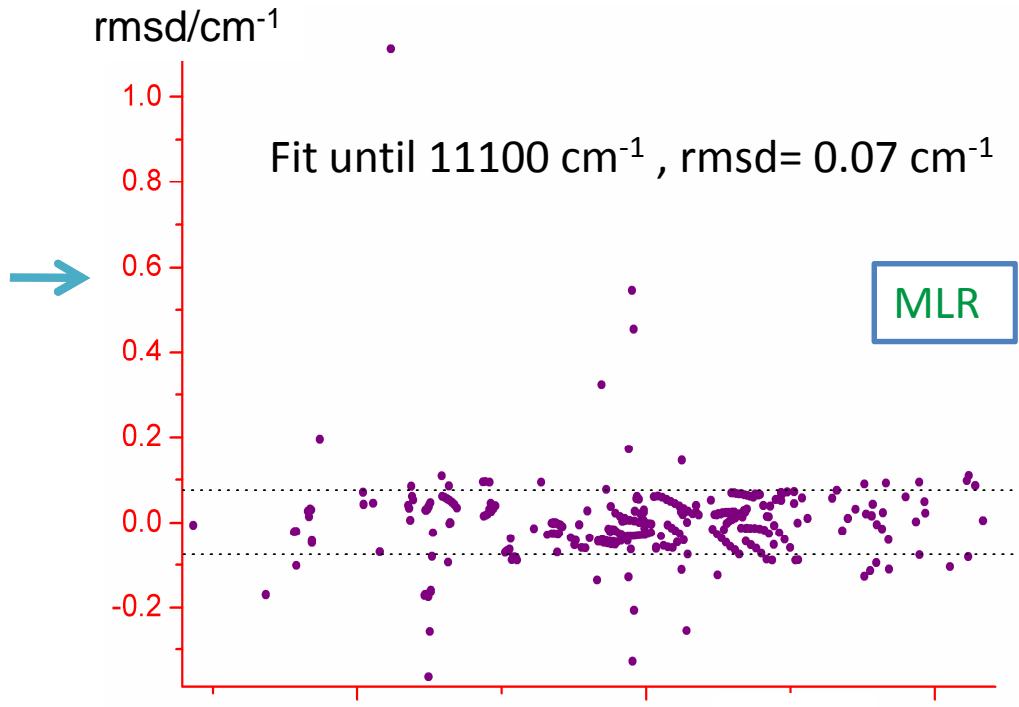
Rms deviation  
(using Hannover potential)  
=  $0.12 \text{ cm}^{-1}$

Potential Energy Curves have been performed using DVR method

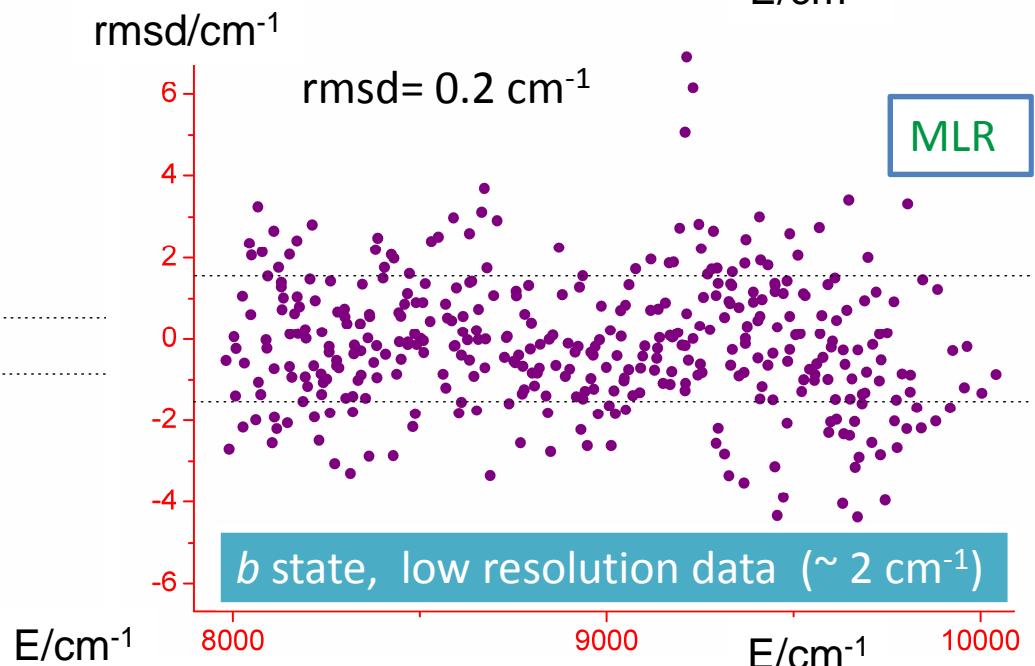
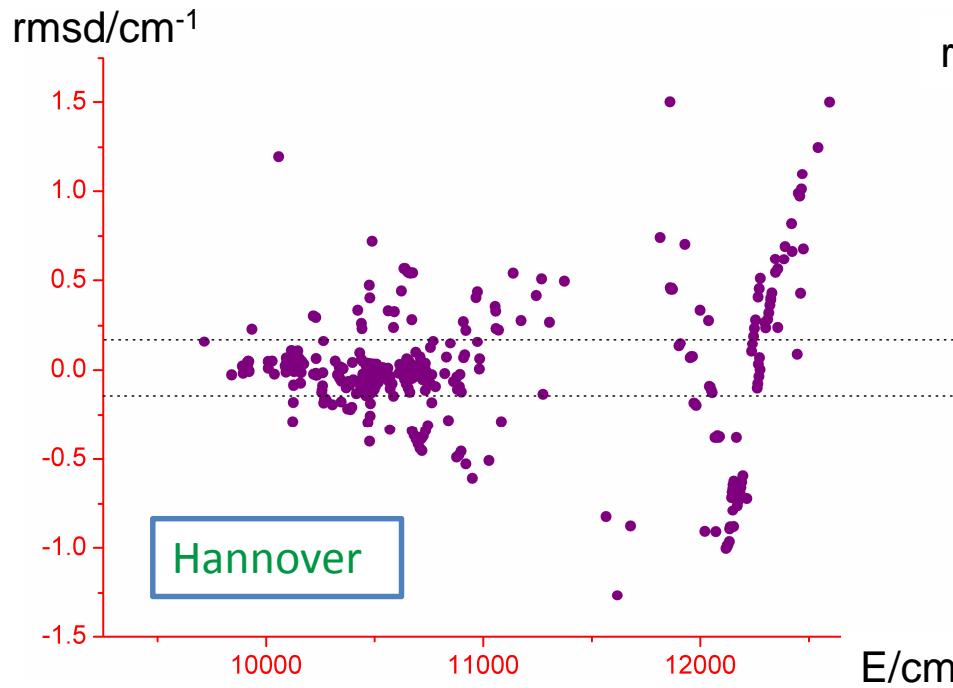
# Fit of the complete data set: Interpolation across the gap



High resolution data on  
the  $A \sim b$  state  
(resolution  $\sim 0.005 \text{ cm}^{-1}$ )



Fit ALL the data, rmsd= 0.2  $\text{cm}^{-1}$



## Acknowledgements

- **Tom Bergeman, State University of New York**



- **Olivier Dulieu, Laboratoire Aimé Cotton**



- **Li Li, Dan Li, Feng Xie, Tsinghua U.**

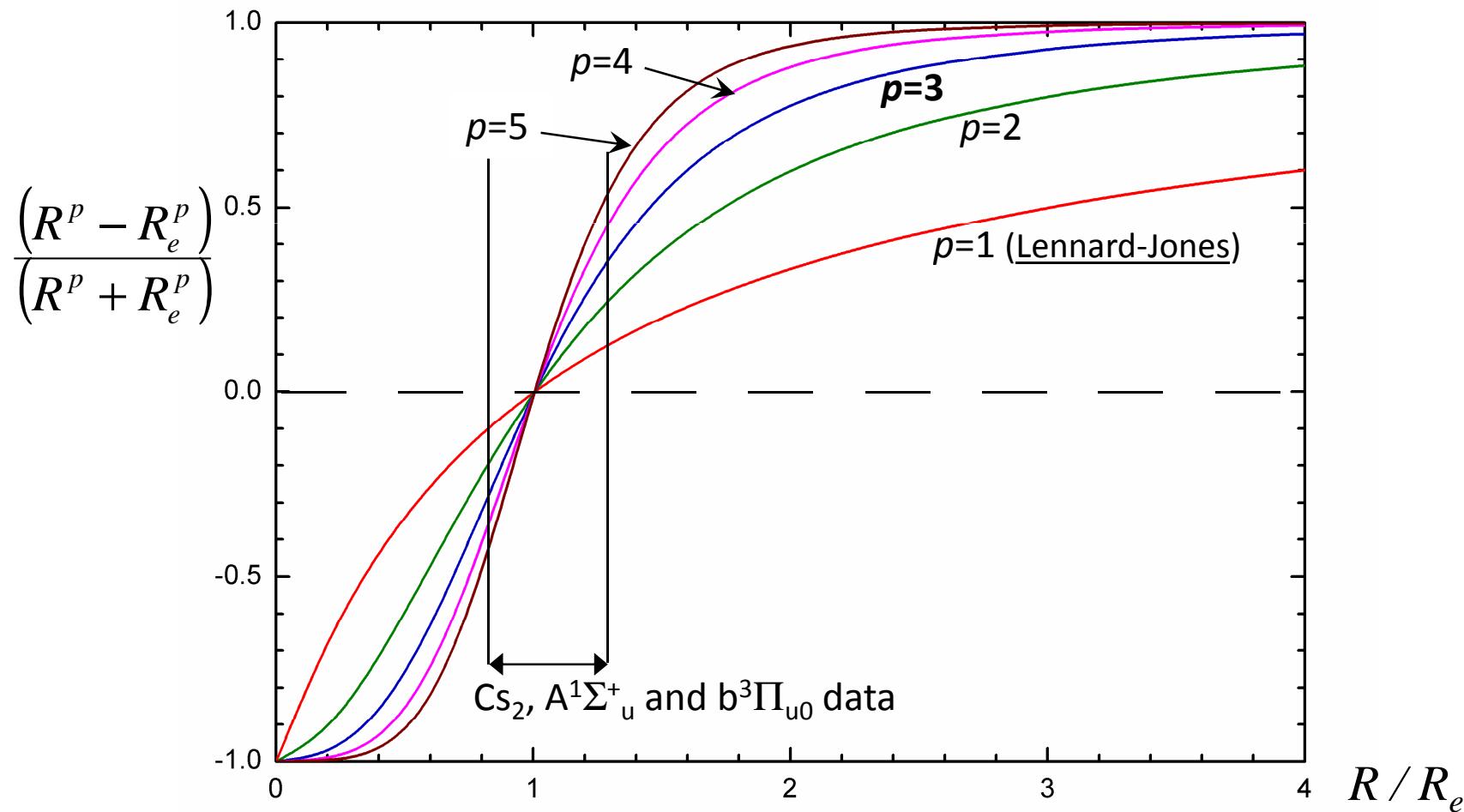


Thank you for your attention



The power  $p$  in the expansion variable  $y_p(R)$  is very important !

- For  $p$  too small, most of the domain  $y_p(R)$  is outside the region where the polynomial in  $y_p(R)$  is determined, so polynomial may *misbehave* there.
- For  $p$  too large,  $y_p(R)$  is too flat in the outer parts of the data region to allow a good fit to the data.



# Term Values

Root mean square =  $0.08 \text{ cm}^{-1}$ , for the high resolution data. (experimental uncertainty =  $0.002 \text{ cm}^{-1}$ )

Rms =  $1.65 \text{ cm}^{-1}$  for the low resolution data ( $\sim$  exp. Uncertainty)

