

**Imposing a Mechanical Model  
on an Irregular Electronic State:  
The  $A^1\Sigma^+$  State of AgH \***

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\* Research supported by the Natural Sciences and Engineering Research Council of Canada.

# Background

- Since its first observation,<sup>1</sup> it has been clear that the  $A\,{}^1\Sigma^+$  state of AgH is highly irregular and/or highly perturbed.
- In 1943 Gerö and Schmidt assigned that irregular behaviour to homogeneous perturbations by the nearby  $B\,{}^1\Sigma^+$  state.<sup>2</sup>
- In 1962 Learner challenged the Gerö-Schmidt interpretation and argued<sup>3</sup>  
*“... that the irregularities of the spectrum, in both position and intensity, may be best explained in terms of an anomalous rotationless potential curve and its associated rotation-including potentials.”*
- Modern diode laser, FTIR and MW experiments accurately define properties of the lower levels for both states.<sup>4</sup>
- Adiabatic and non-adiabatic Born-Oppenheimer breakdown (BOB) effects, which are expected to be significant, were ignored in most previous analyses.

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<sup>1</sup> Bengtsson & Svensson, *Compt. Rend.* **180**, 124 (1925); Hulthén & Zumstein, *Phys. Rev.* **28**, 13 (1926); Bengtsson & Olsson, *Z. Physik* **72**, 163 (1931); Koonts, *Phys. Rev.* **48**, 138 (1935).

<sup>2</sup> Gerö & Schmidt, *Z. Physik* **121**, 459 (1943).

<sup>3</sup> Learner, *Proc. Roy. Soc. (London)* **A 269**, 327 (1962).

<sup>4</sup> Birk & Jones, *Chem. Phys. Lett.* **161**, 27 (1989); Urban *et al.*, *J. Chem. Phys.* **94**, 2523 (1991); Seto *et al.*, *J. Chem. Phys.* **110**, 11756 (1999); Okabayashi & Tanimoto, *J. Mol. Spectrosc.* **204**, 159 (2000).

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- Modern diode laser, FTIR and MW experiments accurately define properties of the lower levels for both states.<sup>8</sup>
- Adiabatic and non-adiabatic Born-Oppenheimer breakdown (BOB) effects, which are expected to be significant, were ignored in most previous analyses.

However ... *we still don't know whether the A-state level spacings are “mechanical” properties of a potential with an unusually shape ... or due to perturbations.*

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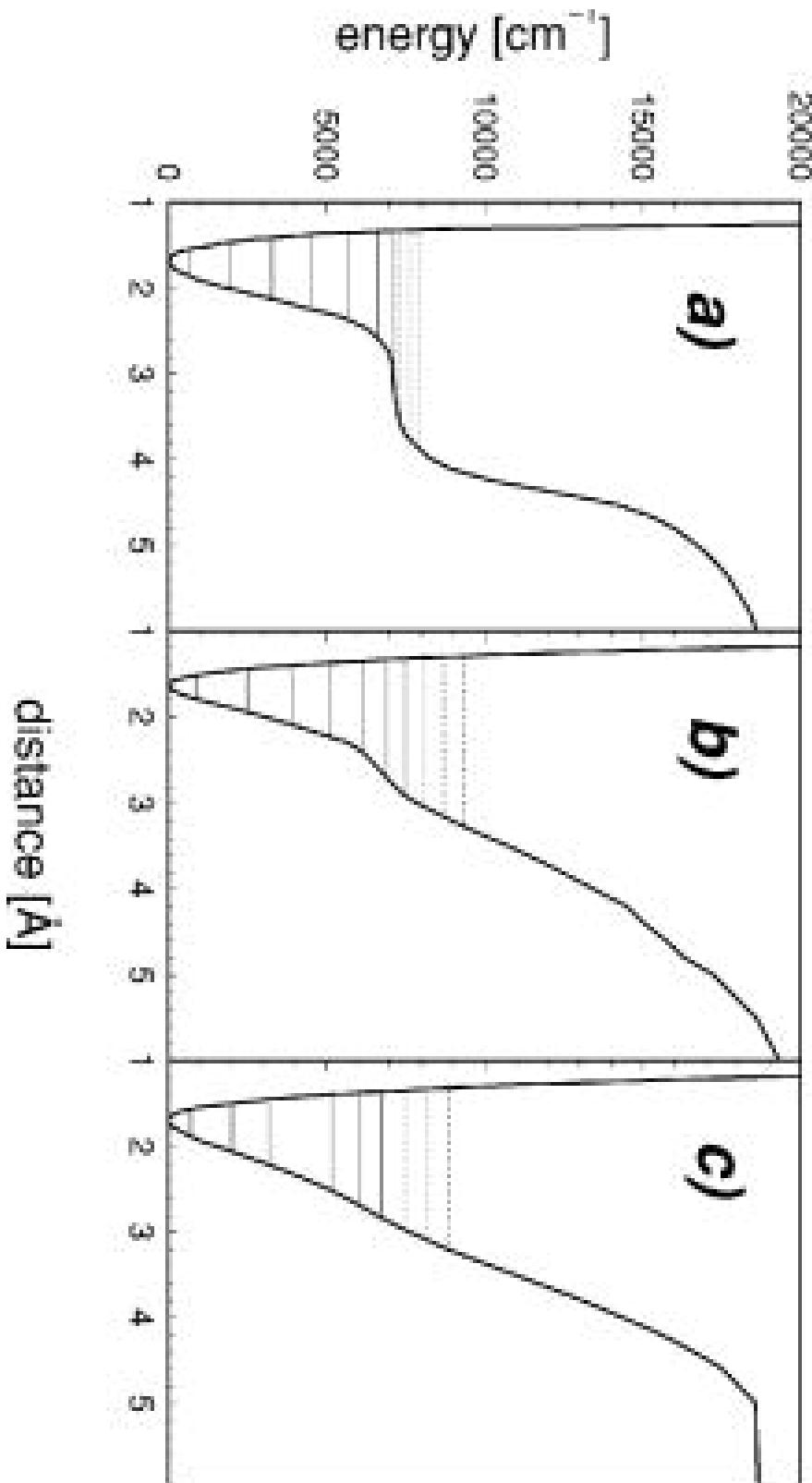
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## *What else is known ?*

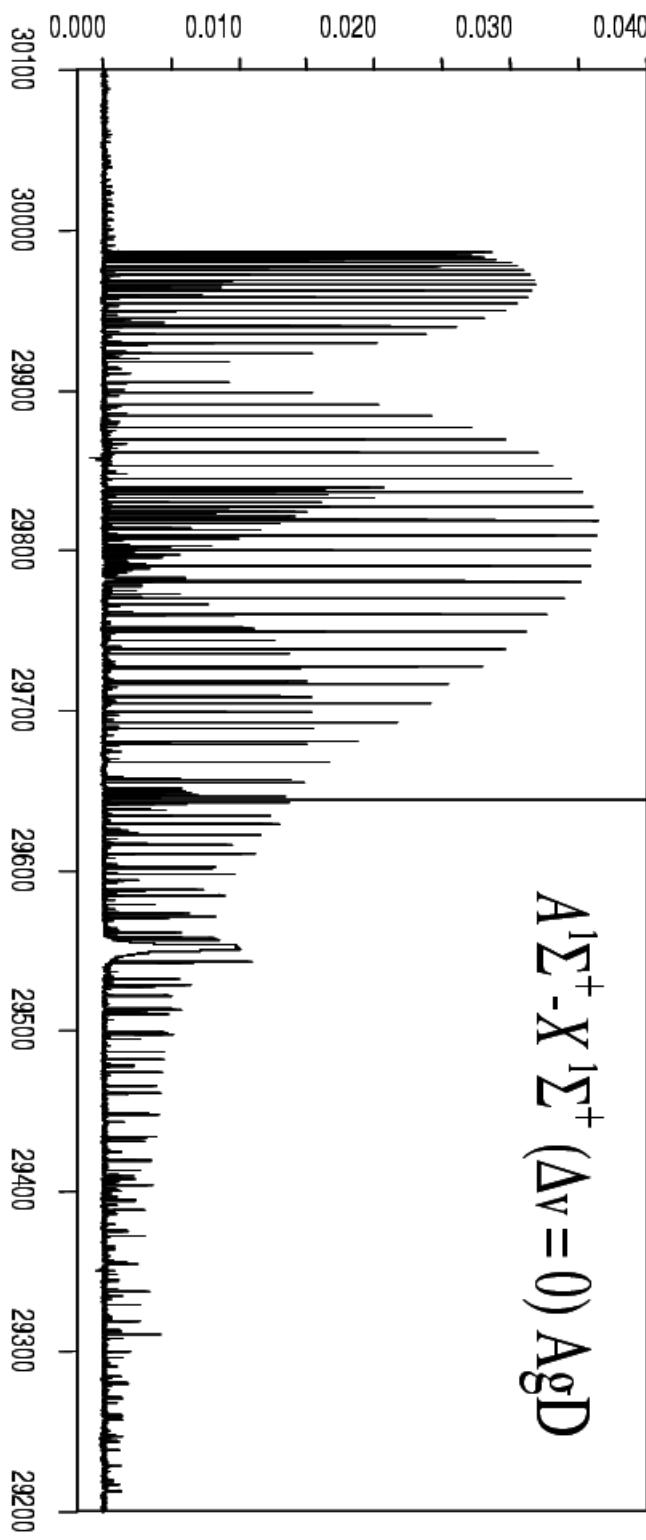
- Learner's (1962) graphical RKR-type method yielded the A-state potential of plot **a)**.<sup>3</sup>
- Witek & co-workers potentials from relativistic *ab initio* calculations are plots **b)** and **c)**.<sup>9</sup>



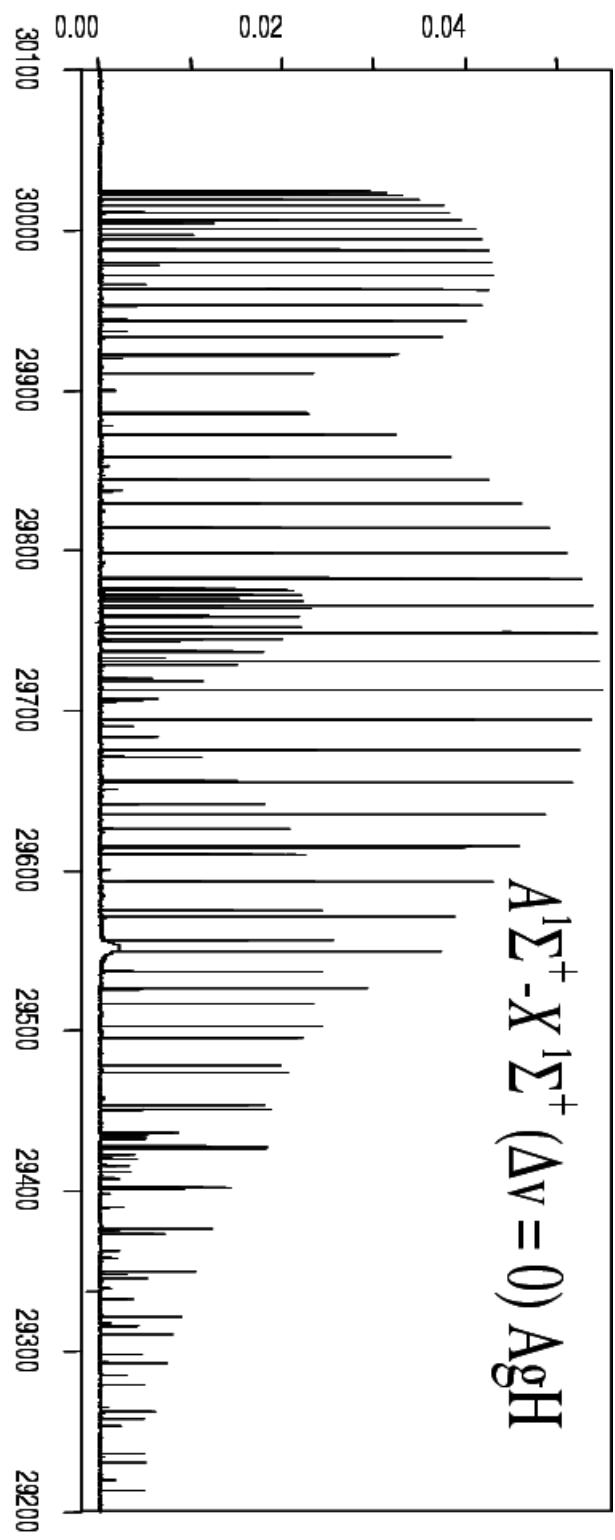
Learner (1962)	Witek <i>et al.</i> (2002)	Witek <i>et al.</i> (2002)
empirical	SO-MCQDPT: CAS- $\alpha$ orbitals	state-averaged orbitals

<sup>9</sup>Witek, Fegorov, Hirao, Viel and Widmark, *J. Chem. Phys.* **116**, 8396 (2002).

wavenumber /cm<sup>-1</sup>



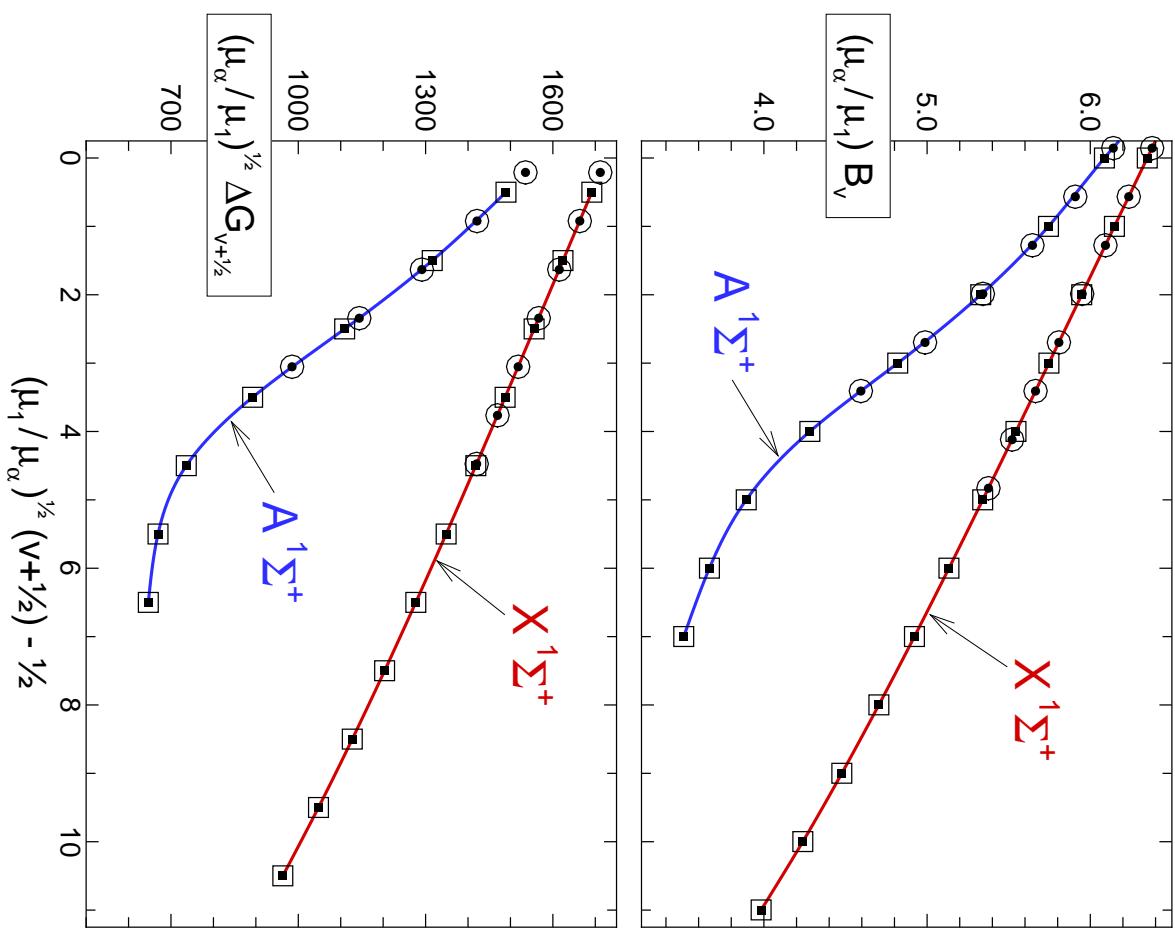
$A^1\Sigma^+ - X^1\Sigma^+$  ( $\Delta v = 0$ ) AgD



$A^1\Sigma^+ - X^1\Sigma^+$  ( $\Delta v = 0$ ) AgD

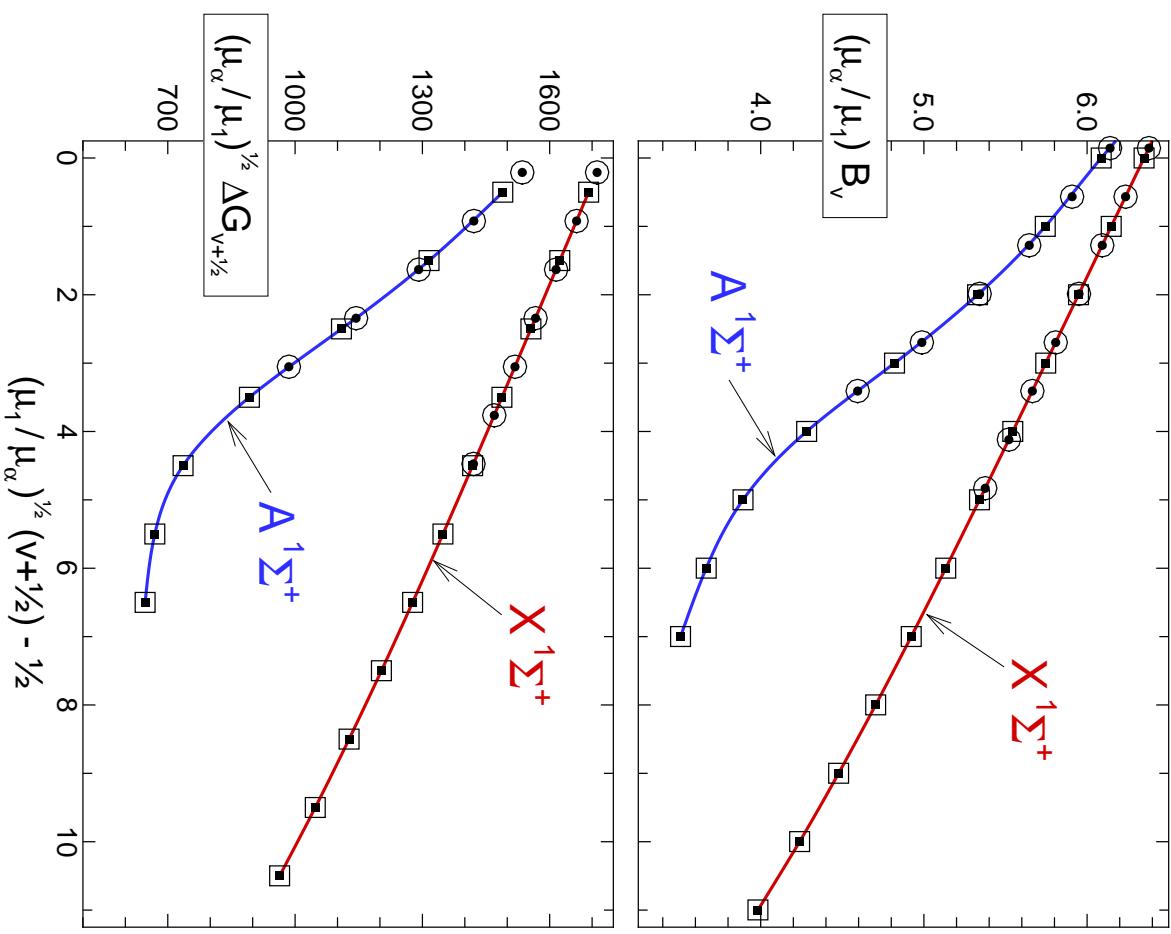
## From a preliminary analysis ...

- Ground state  $\Delta G_{v+1/2}$  &  $B_v$  values vary smoothly and ‘regularly’, but ...
- those for the  $A$  state show unusual  $v$ -dependence; however, ...
- results for AgH (round points) and AgD (square points) fall on the same (mass-scaled) curve ...
- which suggests ... ??



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    - results for AgH (round points) and AgD (square points) fall on the same (mass-scaled) curve ...
    - which suggests ... ??
- that the  $A$ -state might be “mechanical” - with levels defined by some effective radial potential*



## *How Shall We Proceed?*

1. Determine a compete description of the  $X$  state while making no assumptions about the nature of the  $A$  state.
2. Fixing the  $X$ -state, examine increasingly sophisticated models for the  $A$  state.

# How Do We Represent the Data?

term values  $T_{v,J}^{(\alpha)}$ :

$$E(v, J) = T_{v,J}^{(\alpha)}$$

band constants  $K_m^{(\alpha)}(v)$ :

$$\begin{aligned} E(v, J)^{(\alpha)} &= T_e^{(\alpha)} + G_v^{(\alpha)} + B_v^{(\alpha)}[J(J+1)] - D_v^{(\alpha)}[J(J+1)]^2 + H_v^{(\alpha)}[J(J+1)]^3 + \dots \\ &= T_e^{(\alpha)} + \sum_{m=0} K_m^{(\alpha)} [J(J+1)]^m \end{aligned}$$

Dunham parameters  $Y_{l,m}^{(\text{ref})}$ :

$$E(v, J)^{(\alpha)} = T_e^{(\alpha)} + \sum_{m=0} \sum_{l=0} Y_{l,m}^{(\text{ref})} \left( \frac{\mu_{\text{ref}}}{\mu_\alpha} \right)^{m+l/2} (v + \frac{1}{2})^l [J(J+1)]^m$$

potential function  $V(R; \{p_i\})$

*all vibration-rotation levels are numerically-determined eigenvalues of some parameterized analytic potential function*

**First fit to the X state alone** while representing A-state levels by term values

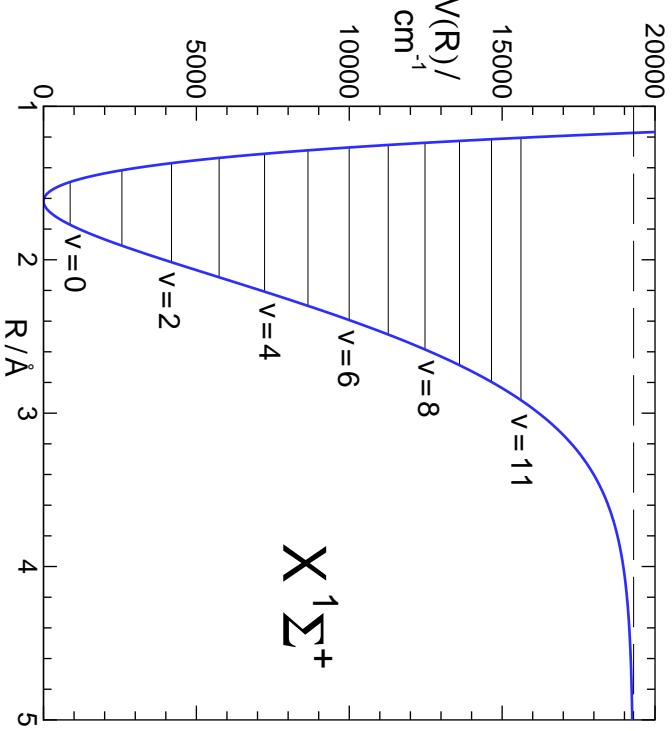
X-state model	$\mathfrak{D}_e$	$N_{\text{Ham}}$	$N_{\text{tot}}$	$\overline{dd}$	no. param.
all Dunham:	n/a	31	942	0.909	
EMO <sub>3</sub> potential:	19235 ( $\pm 3.4$ )	15	926	0.92	
MLJ <sub>3</sub> potential:	19329 ( $\pm 1.5$ )	16	927	0.99	$V(R)/\text{cm}^{-1}$
MLJ <sub>3</sub> potential:	19354 ( $\pm 2.7$ )	17	928	0.93	10000
MLJ <sub>2</sub> potential :	19300 ( $\pm 6.6$ )	16	927	0.94	$v=11$
					$v=8$
					$v=6$
					$v=4$

$$V_{\text{EMO}_p}(R) = \mathfrak{D}_e [1 - e^{-\beta(y_p) \cdot (R - R_e)}]^2$$

$$\text{where } y_p = y_p(R) = \frac{R^p - R_e^p}{R^p + R_e^p}$$

$$V_{\text{MLJ}_p}(R) = \mathfrak{D}_e \left[ 1 - \left( \frac{R_e}{R} \right)^n e^{-\beta(y_p) \cdot y_p(R)} \right]^2$$

$$\simeq \mathfrak{D}_e - \frac{C_n}{R^n}$$



**First fit to the X state alone** while representing A-state levels by term values

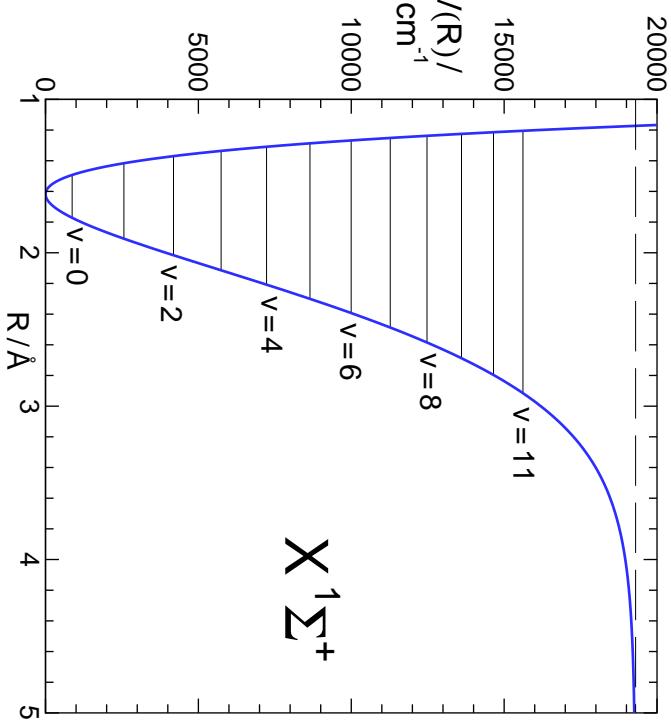
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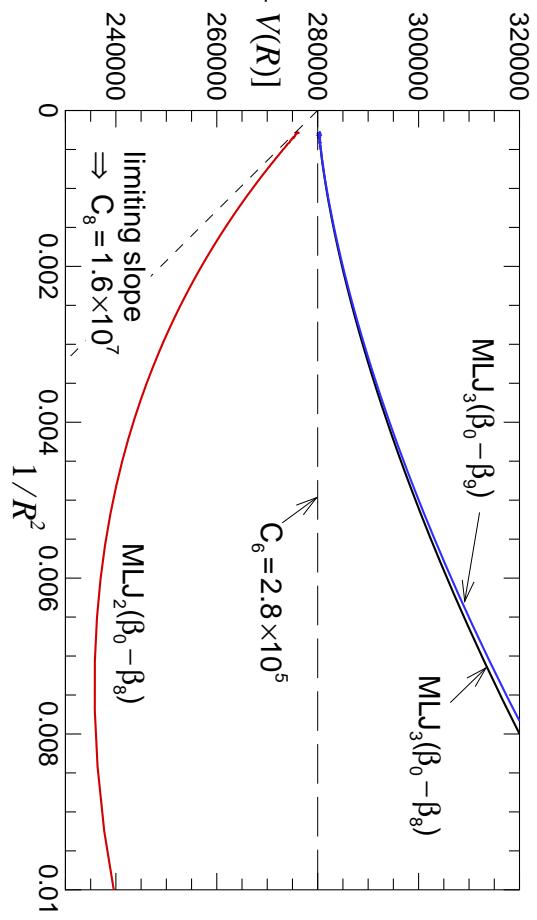
$$\simeq \mathfrak{D}_e - \frac{C_n}{R^n}$$



But for an MLJ<sub>p</sub> potential

$R^n \times [\mathfrak{D}_e - V(R)]$  should approach  $C_n$  from below!

*so the MLJ<sub>2</sub> function is best!*



**Now ... “parameter” fits to  
both States simultaneously**

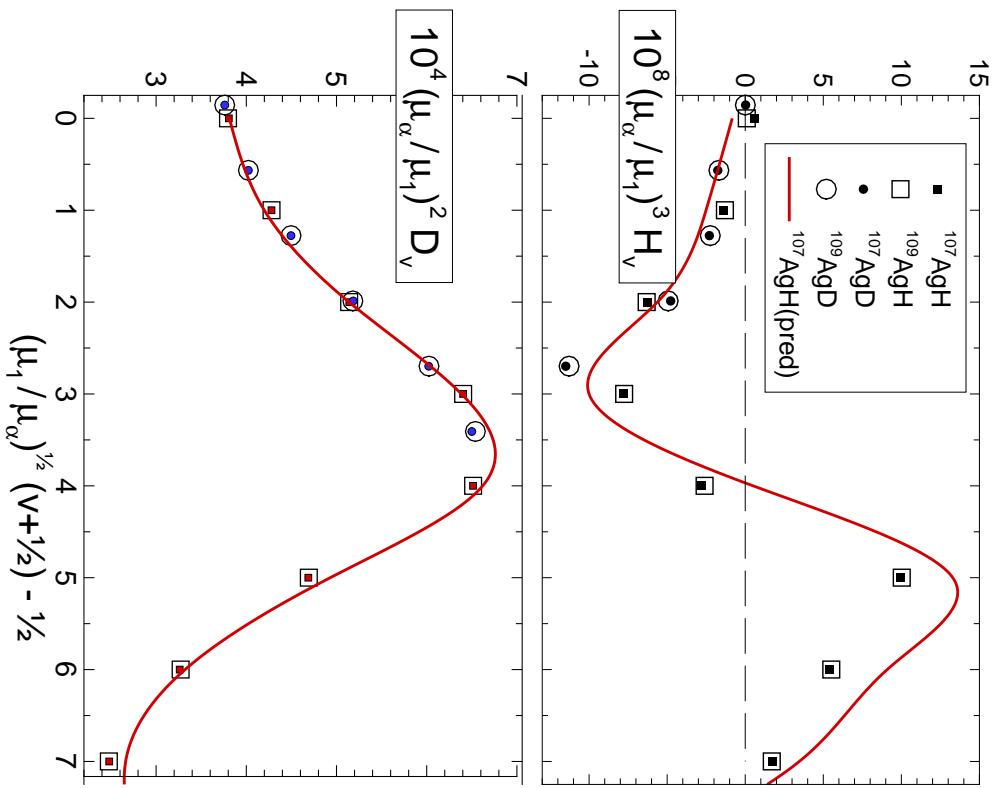
Using our 31-parameter  
Dunham model for the  $X$ -state:

$X$ -state model	$A$ -state model	no. param.	$\overline{dd}$
		$N_{\text{Ham}} (N_{\text{tot}})$	
31 Dunham param.	term values $T_{v,J}^{(\alpha)}$	31 (942)	0.91
31 Dunham param.	all band constants	195	1.13
31 Dunham param.	Dunham for $G_v$ plus rotational band constants	182	1.14
31 Dunham param.	Dunham for $G_v$ & $B_v$ plus CDC band constants	166	1.15

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**$X$ -state model       $A$ -state model**

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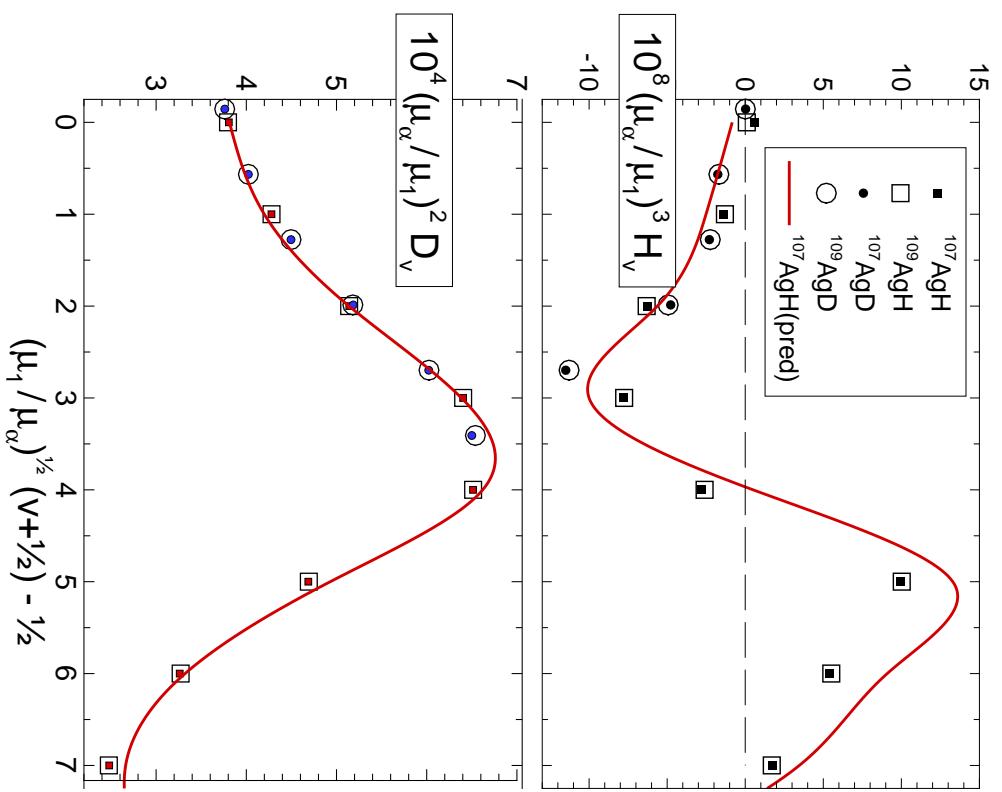
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31 Dunham param.	all Dunham : 64 $Y_{l,m}$ and 30 BOB parameters	125      1.13

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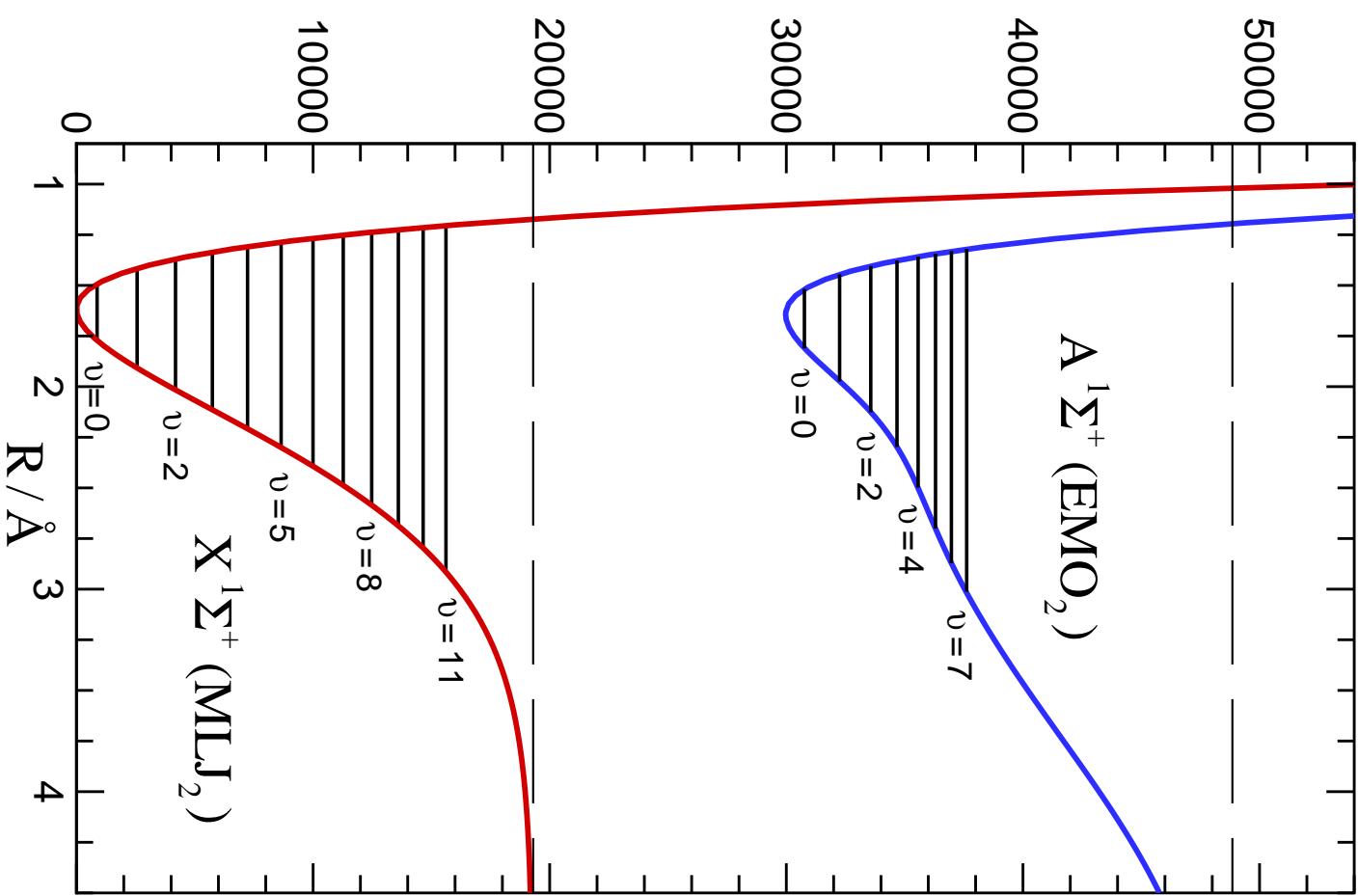
- This suggests:
- the  $A$  state may have an irregular shape, but ...
  - it is not “perturbed”, in that ...
  - its levels are eigenvalues of an effective radial potential function!



$X$ -state model	$A$ -state model	no. param.
31 Dunham param.	term values $T_{v,J}^{(\alpha)}$	31 ( $N_{\text{tot}} = 942$ )
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*Finally ... direct potential fits  
to both states simultaneously!*

X-state	A-state	# parm.	$\overline{dd}$
Dunham	term values	942	0.91
MLJ <sub>2</sub> (8, 8)	term values	927	0.94
Dunham	Dunham	125	1.13
MLJ <sub>2</sub> (8, 8)	EMO <sub>3</sub> (4, 9)	39	1.53
MLJ <sub>2</sub> (8, 8)	EMO <sub>3</sub> (4, 10)	40	1.45



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## Conclude

The A  $^1\Sigma^+$  state of AgH is “mechanical”, since its level spacings are explained by an effective radial potential plus adiabatic & non-adiabatic radial correction functions.

