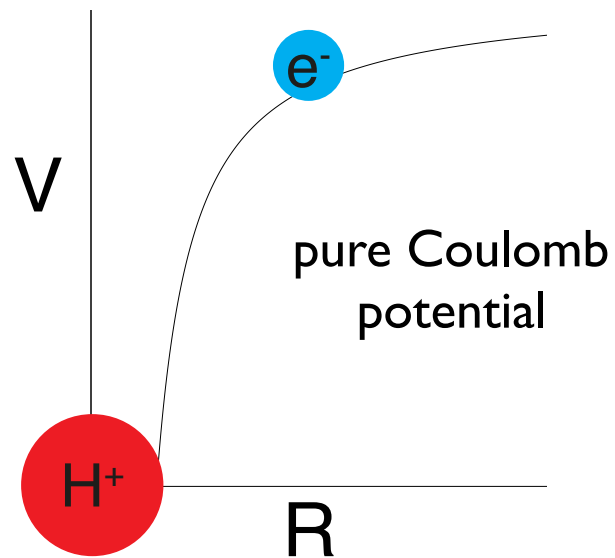


Heavy Rydberg states in H₂ and HD

Maximilian Beyer and Frédéric Merkt

Rydberg states

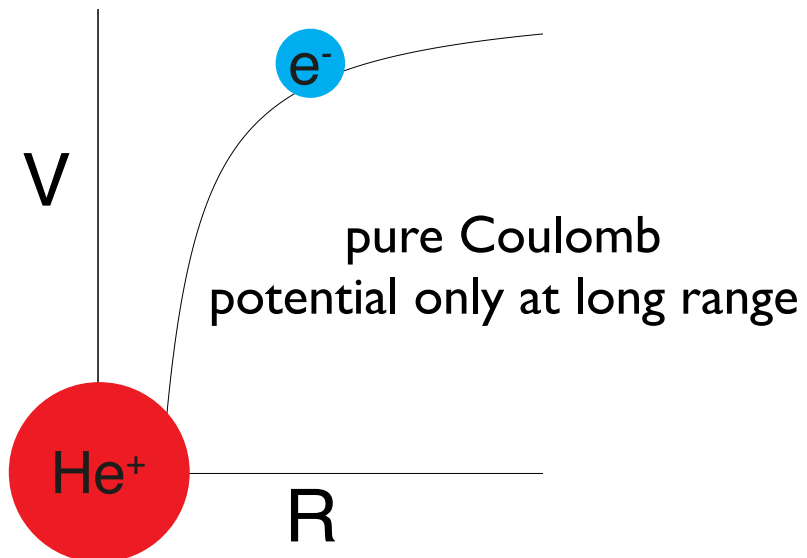
Hydrogen atom



$$\mathcal{R}_H = 109'677.58 \text{ cm}^{-1}$$

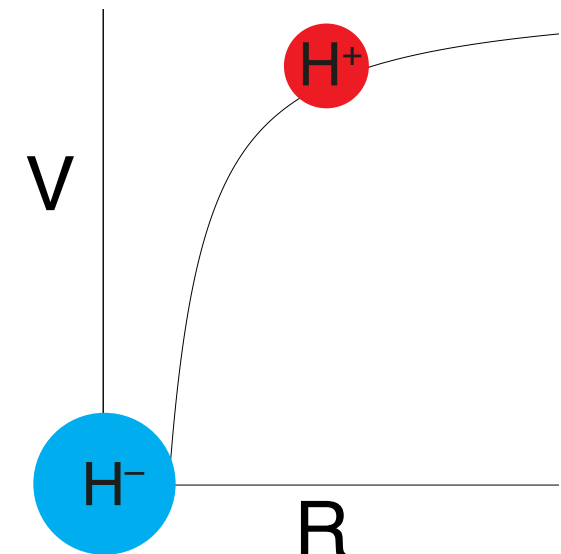
$$E_n = E_I - \frac{\mathcal{R}_\infty \mu / m_e}{n^2}$$

Helium atom



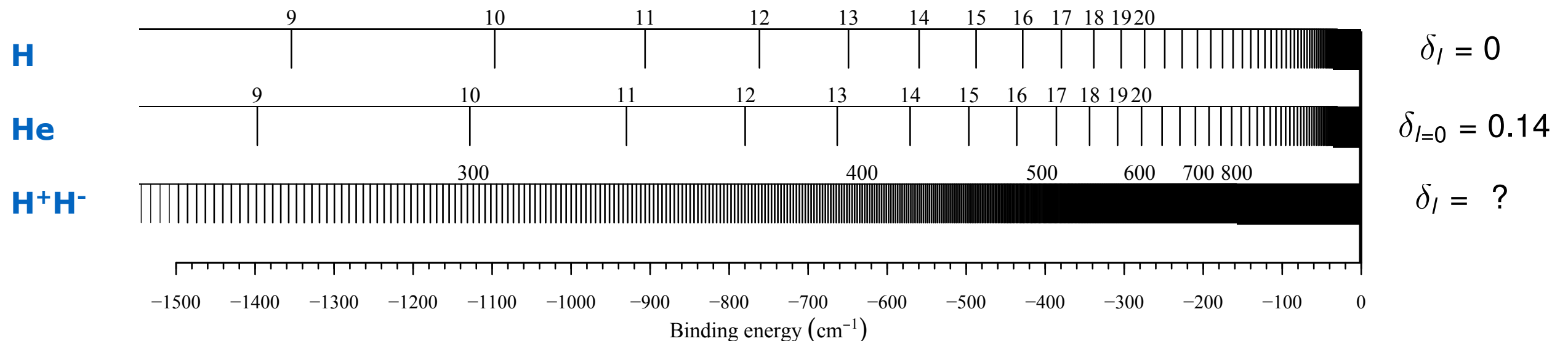
$$\mathcal{R}_{\text{He}} = 109'722.28 \text{ cm}^{-1}$$

H^+H^-



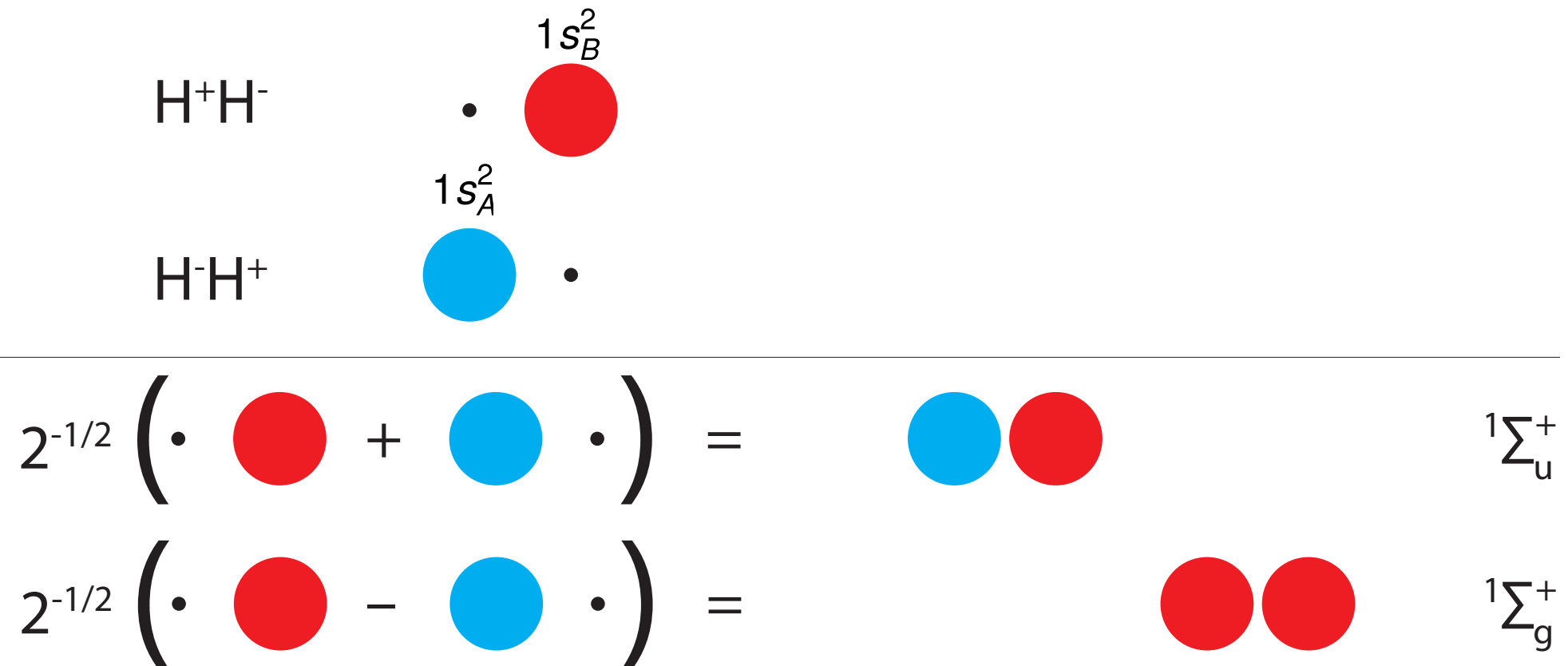
$$\mathcal{R}_{\text{H}^+\text{H}^-} = 100'802'071.60 \text{ cm}^{-1}$$

$$E_{nl} = E_I(\alpha^+) - \frac{\mathcal{R}_\infty \mu / m_e}{(n - \delta_l)^2}$$



Ion-pair states

- Molecular states at the H^+H^- and H^-H^+ dissociation threshold



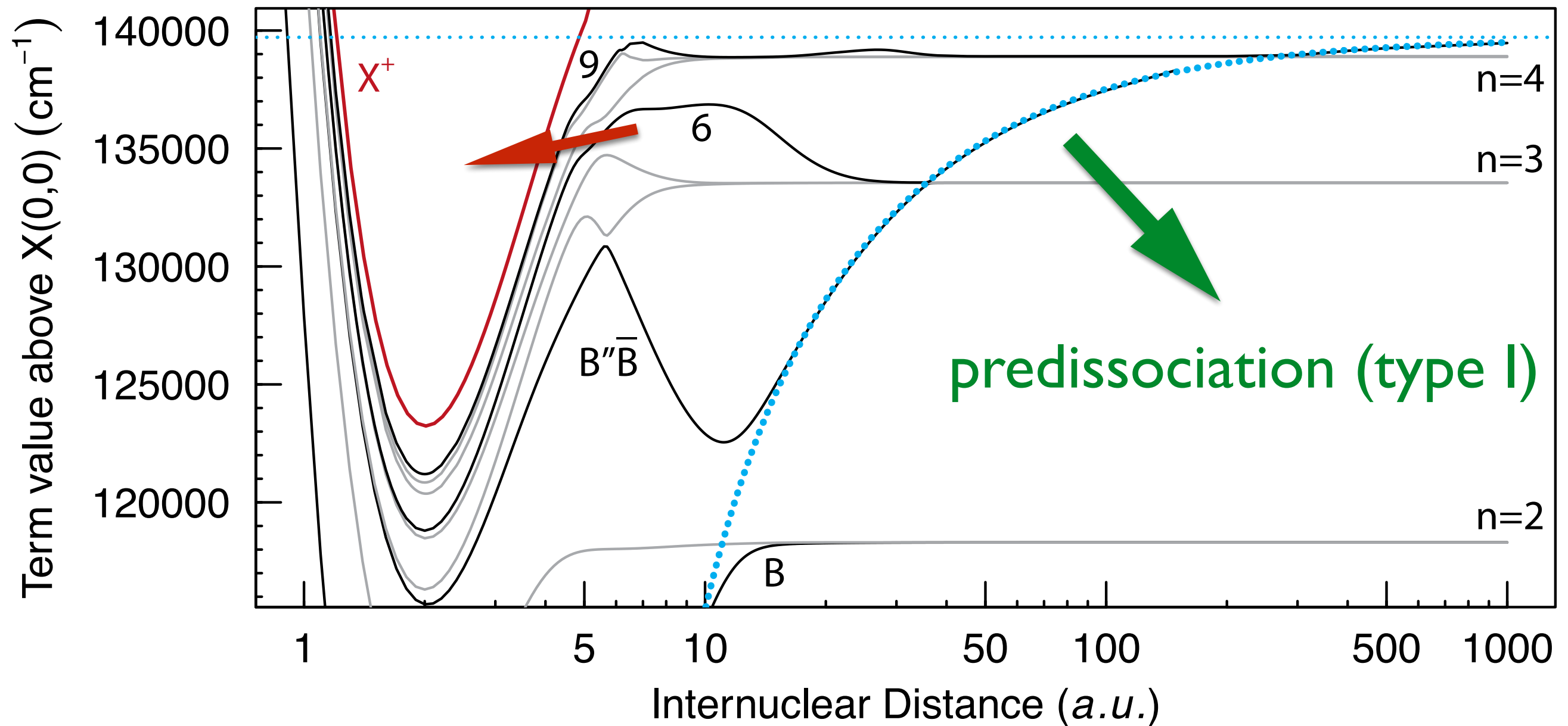
- Perturbations of other molecular states via homogeneous ($\Sigma^+ - \Sigma^+$) and heterogeneous ($\Sigma^+ - \Pi^+$) nonadiabatic interactions

➔ More about g/u mixing in **TB04**

Ion-pair states

autoionization

$1 - 9 \ ^1\Sigma_u^+$ states

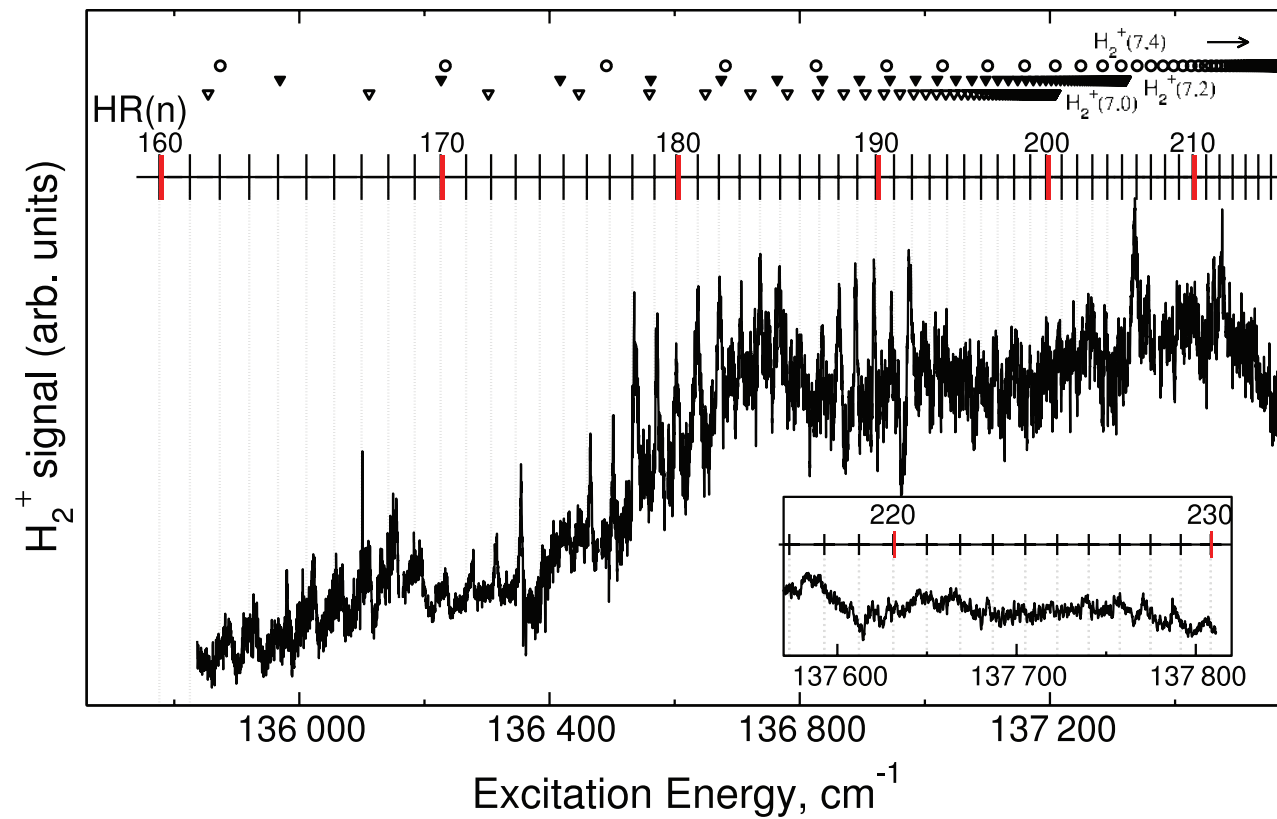


Detmer, Schmelcher and Cederbaum, *J. Chem. Phys.* **109**, 9694 (1998)

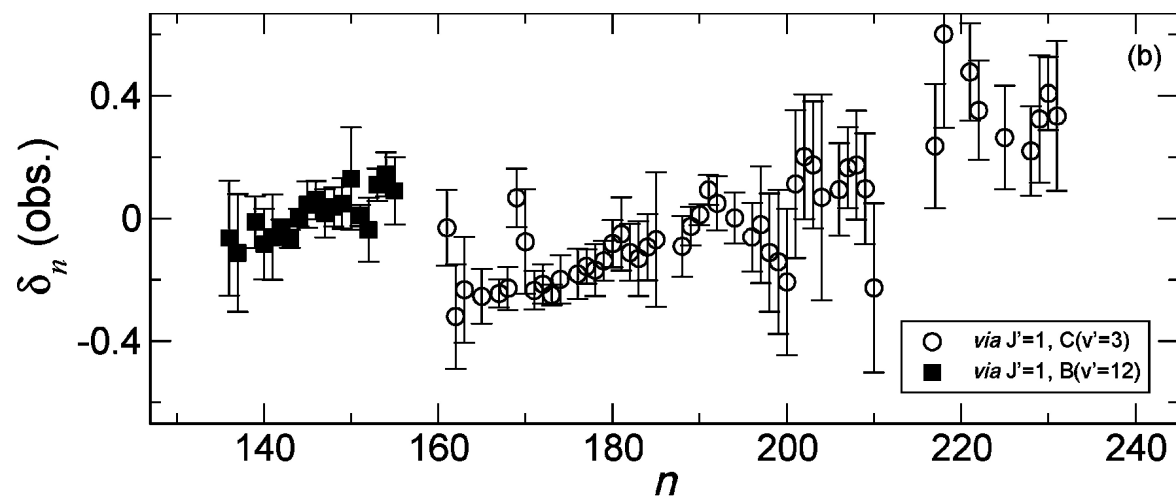
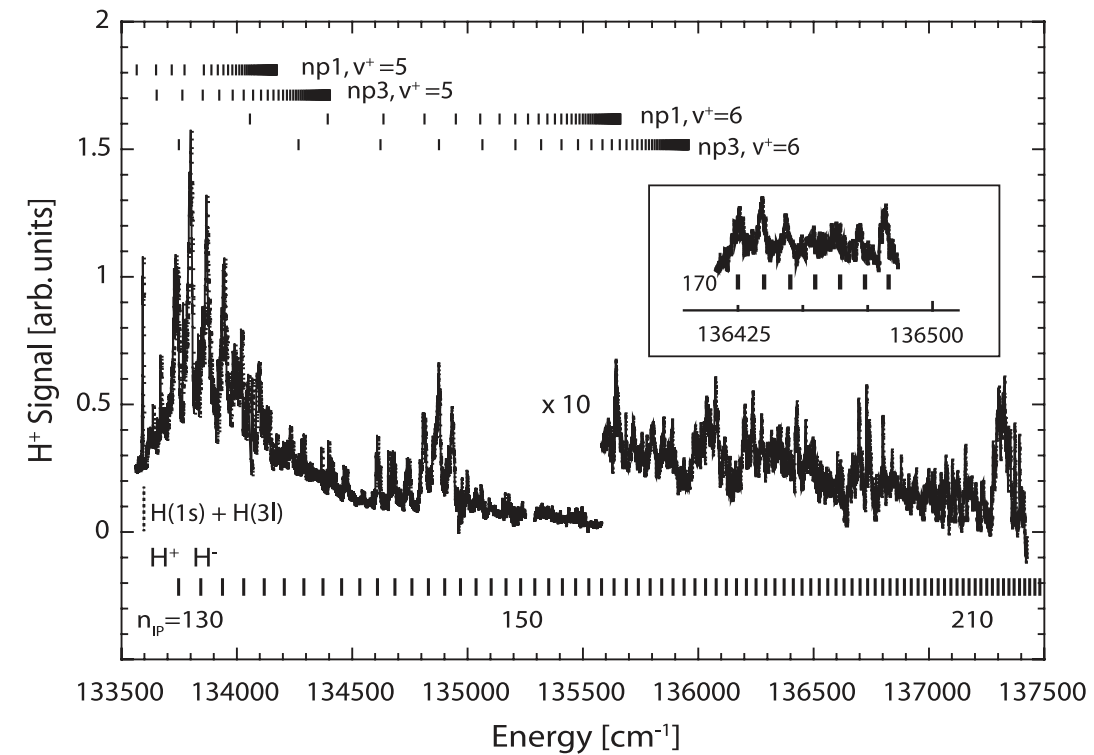
Staszewska and Wolniewicz, *J. Mol. Spectrosc.* **212**, 208 (2002)

Observation of heavy Rydberg states in H₂ with $n < 230$

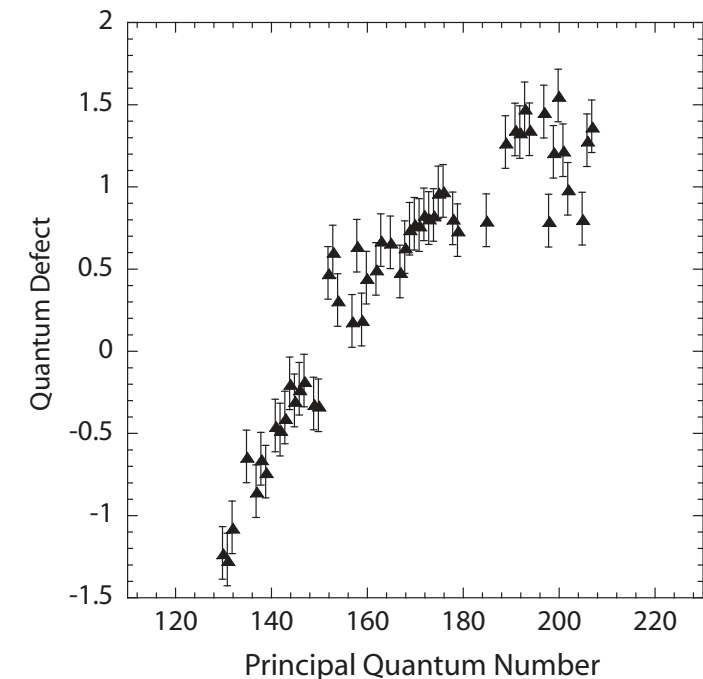
gerade symmetry



ungerade symmetry



energy-dependent
quantum defect



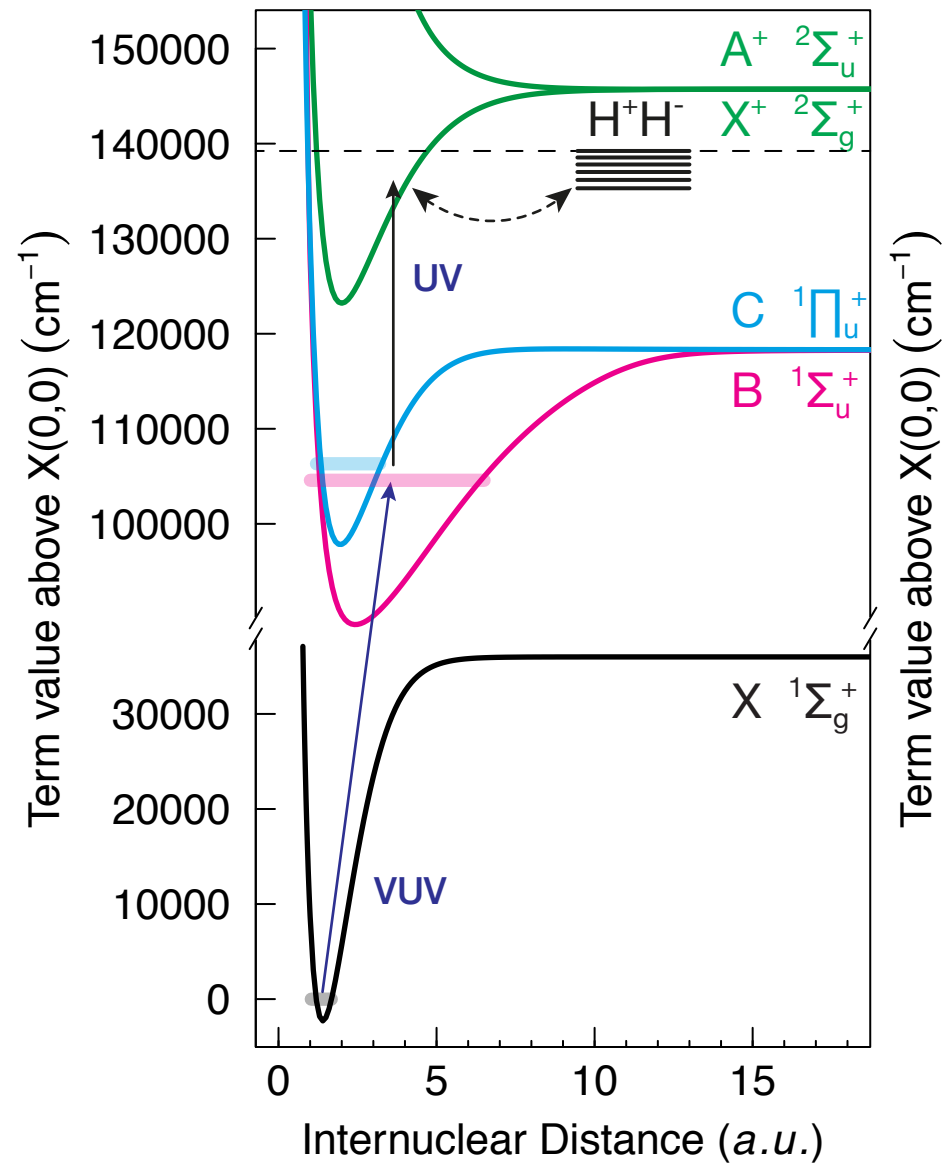
Vieitez, Ivanov, Reinhold, de Lange and Ubachs, *Phys. Rev. Lett.* **101**, 163001 (2008)

Vieitez, Ivanov, Reinhold, de Lange and Ubachs, *J. Phys. Chem. A* **113**, 13237 (2009)

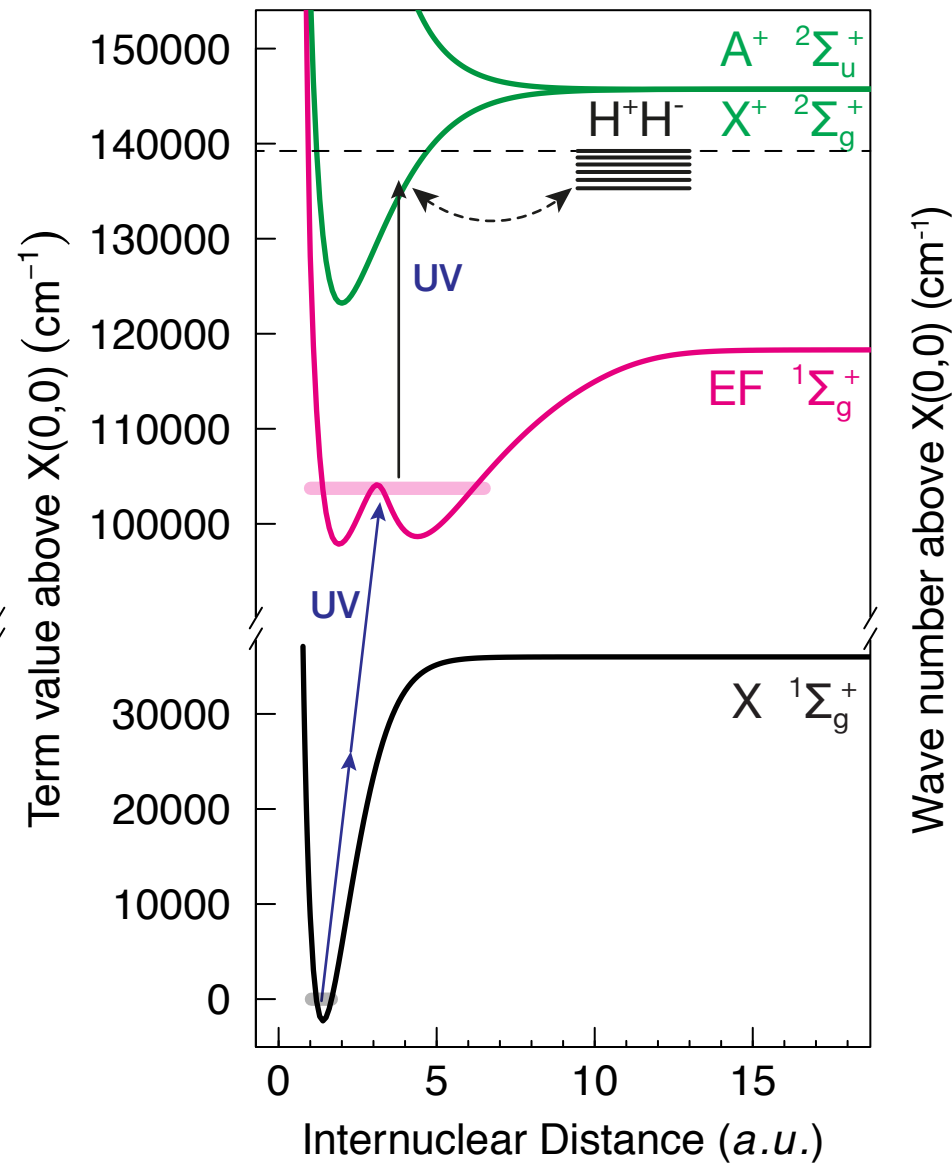
Ekey Jr and McCormack, *Phys. Rev. A* **84**, 020501(R) (2011)

Excitation of heavy Rydberg states

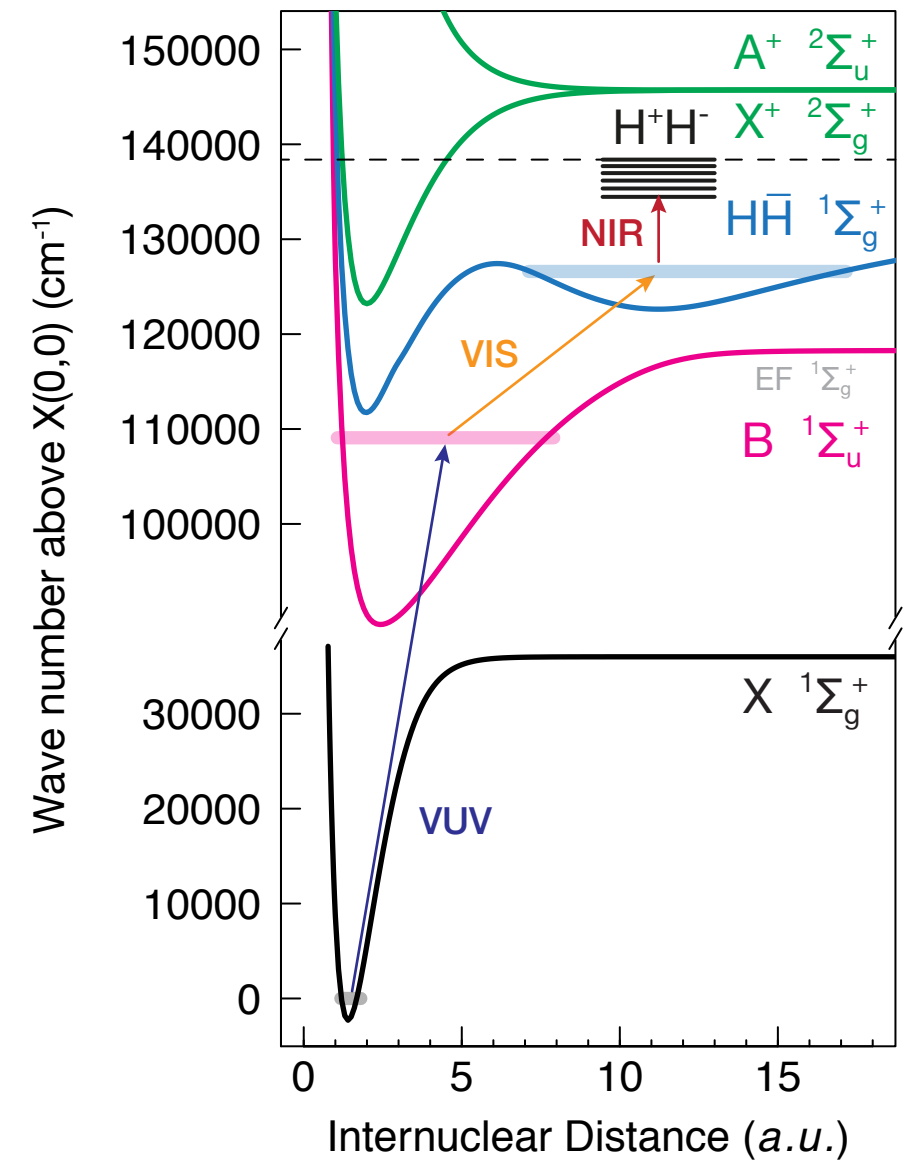
Ubachs group



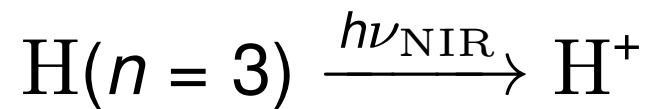
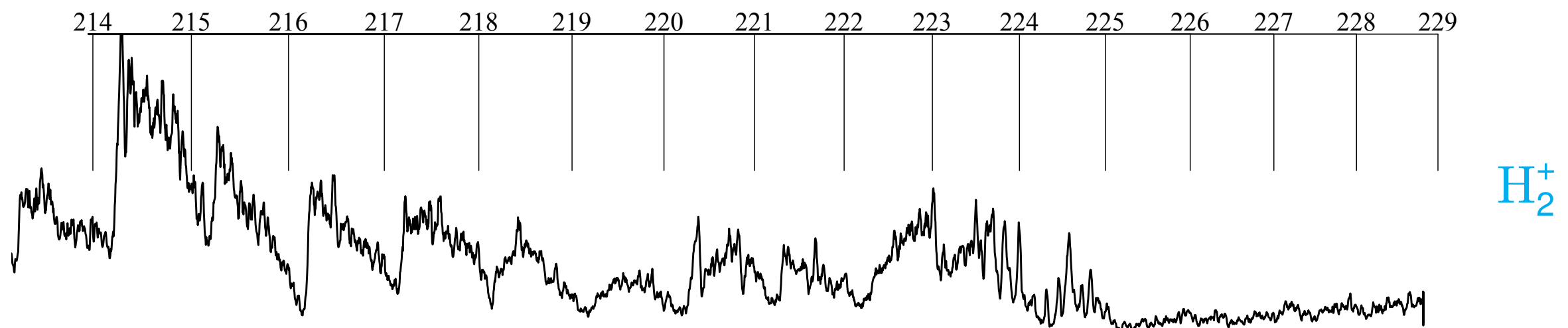
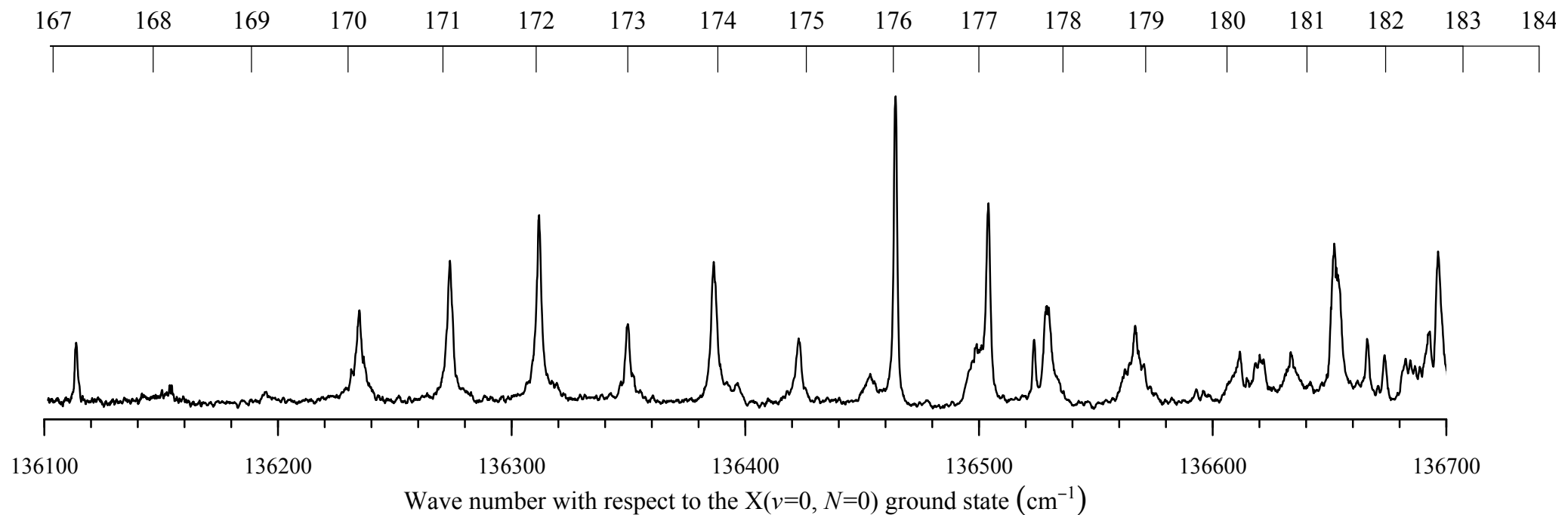
McCormack group



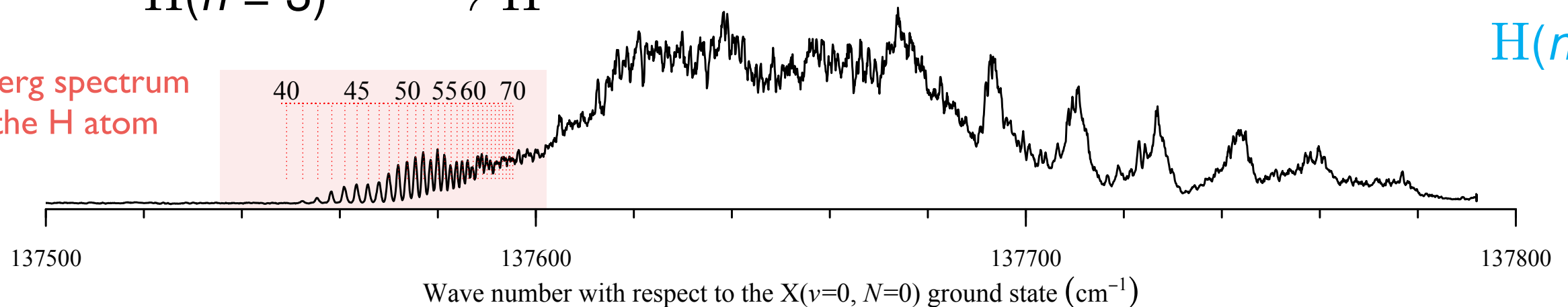
Our approach



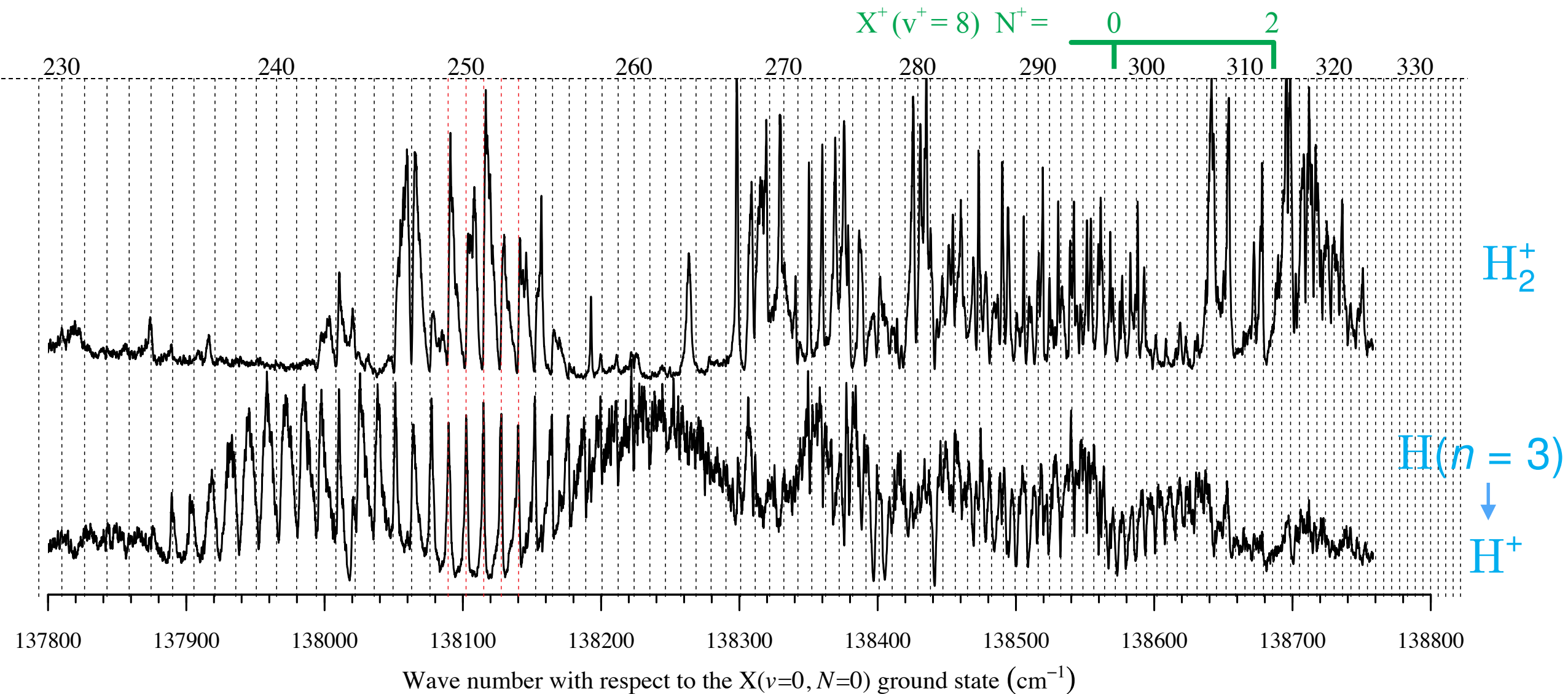
low- n H^+H^- heavy Rydberg states



Rydberg spectrum
of the H atom

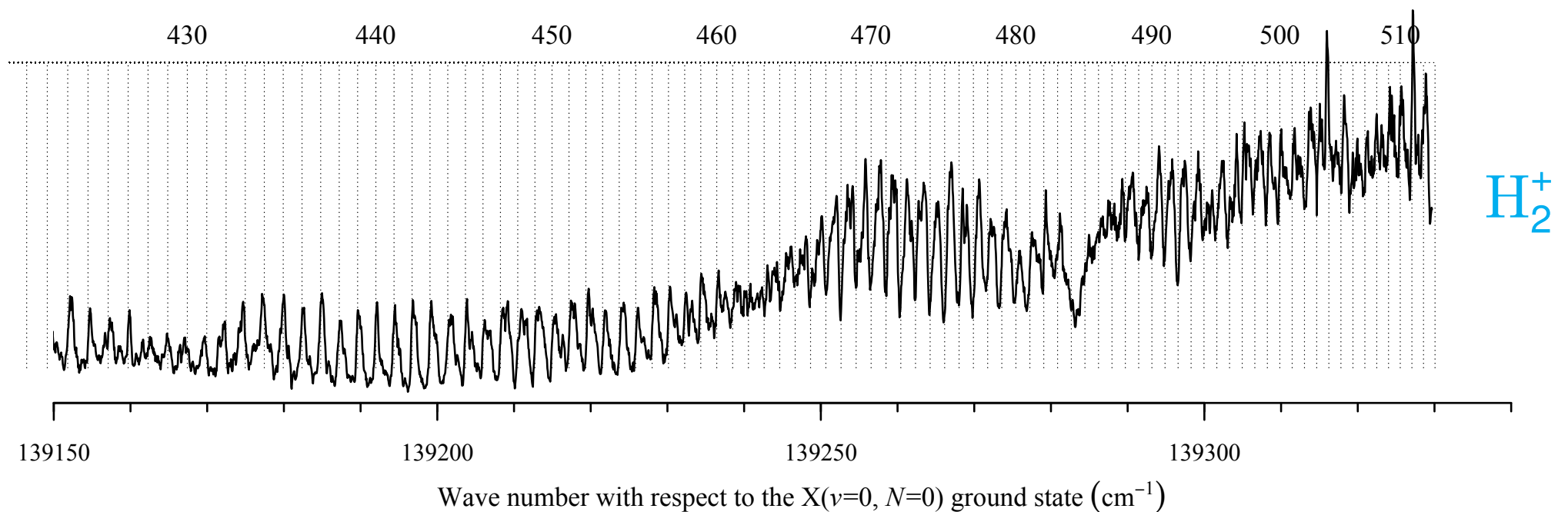


high- n H^+H^- heavy Rydberg states

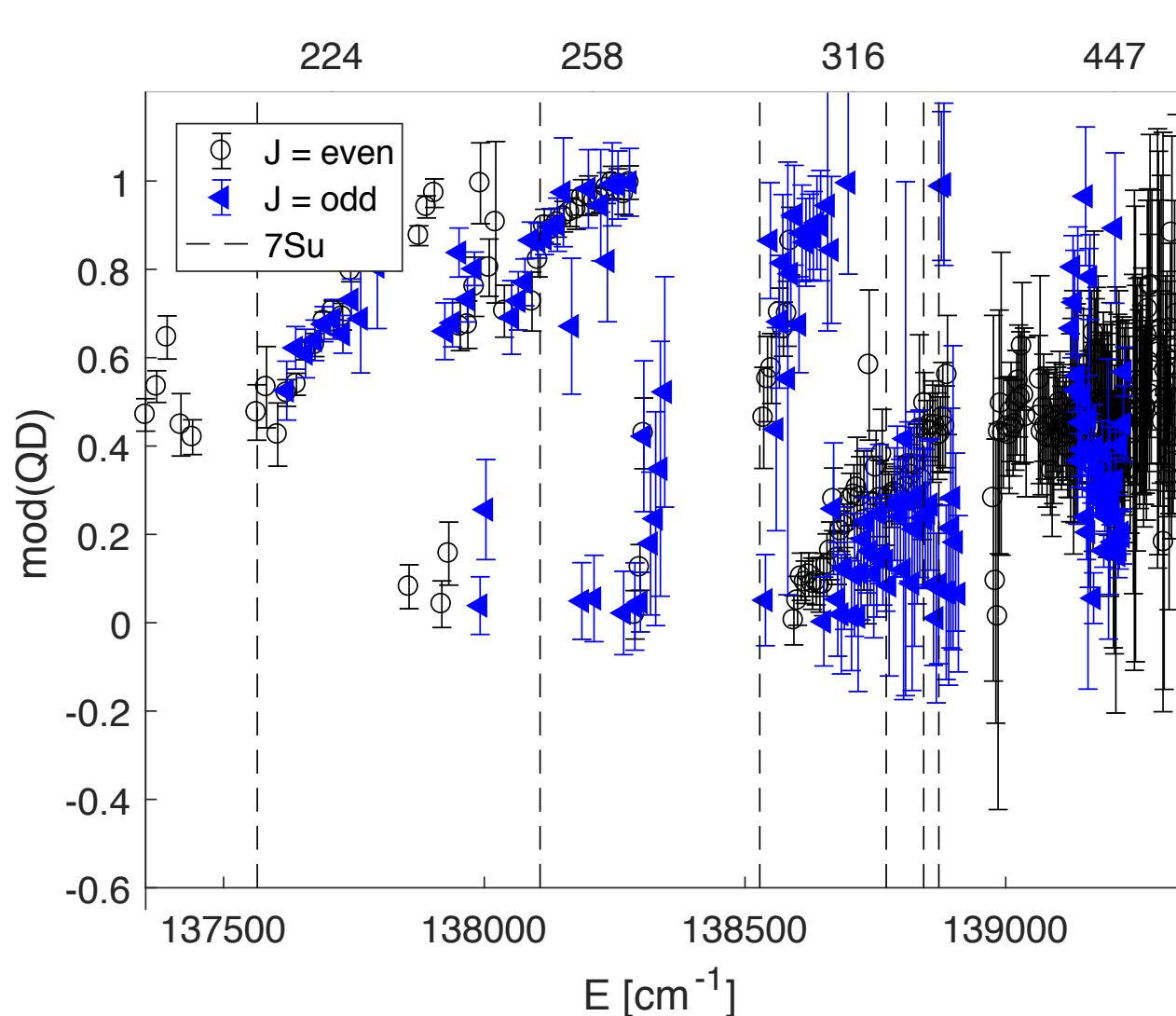


@ $n=500$

- classical turning point: $544 a_0$
- Kepler radius: $270 a_0$



Quantum defects

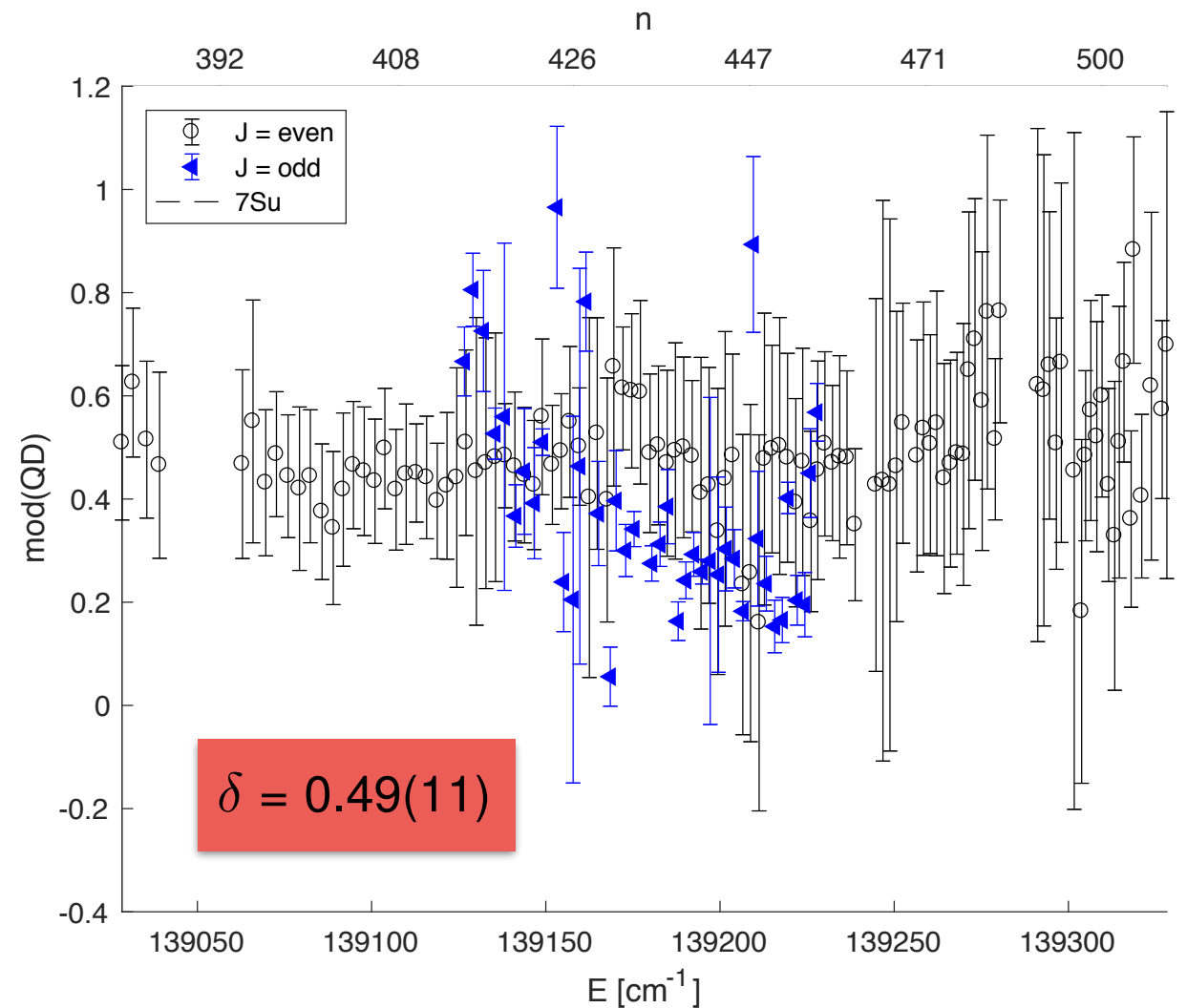


$$\text{IP}(\text{H}^+\text{H}^-) = D_0(\text{H}_2) + \text{IP}(\text{H}) - \text{EA}(\text{H})$$

$$139713.85(16) \text{ cm}^{-1}$$

$$\text{EA}(\text{H}) = 6082.99(15) \text{ cm}^{-1}$$

Lykke, Murray and Lineberger, *Phys. Rev. A* **43**, 6104 (1991)



Extrapolation of series limit:

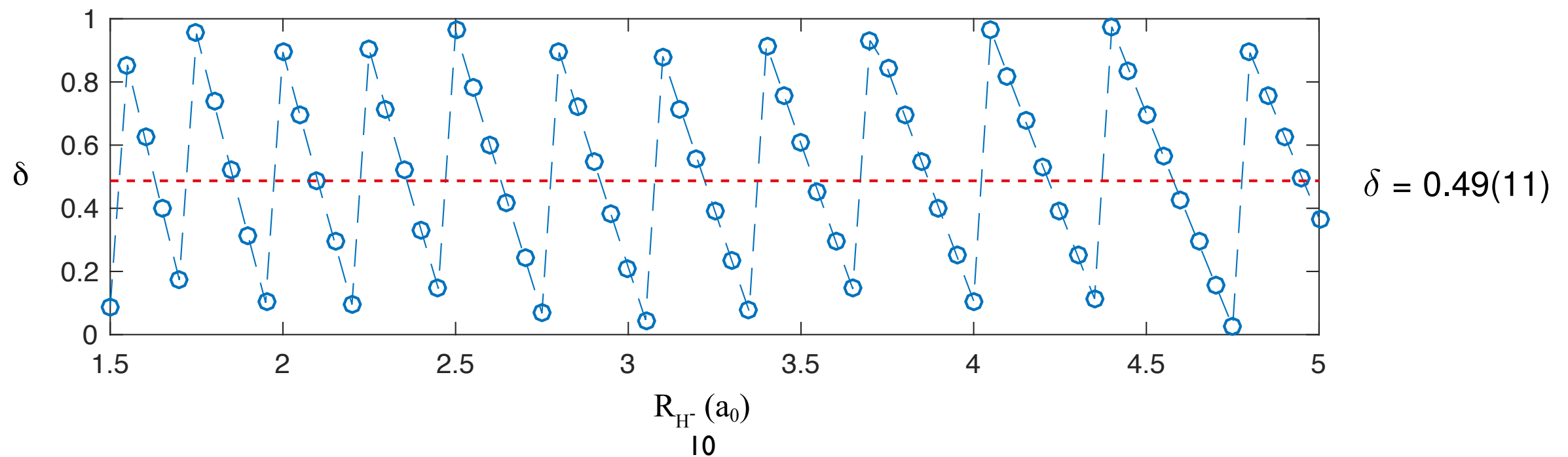
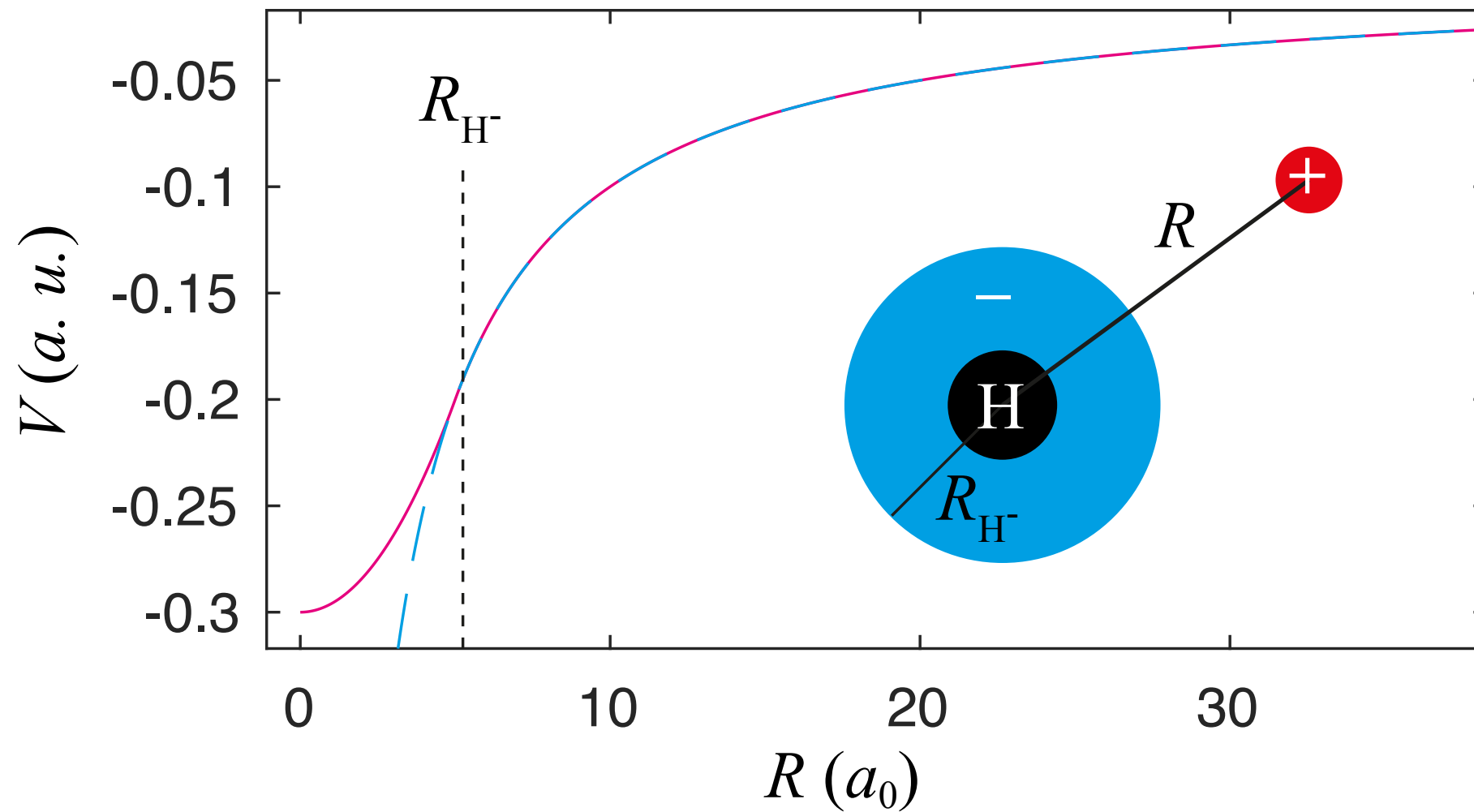
preliminary
result

$$139713.89(23) \text{ cm}^{-1}$$

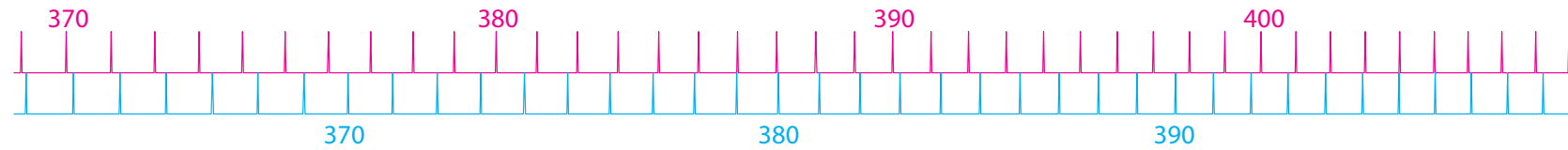
uncertainty of the intermediate $\bar{\text{H}}$ state: 0.06 cm^{-1}

Reinhold, Hogervorst and Ubachs, *Phys. Rev. A* **60**, 1258 (1999)

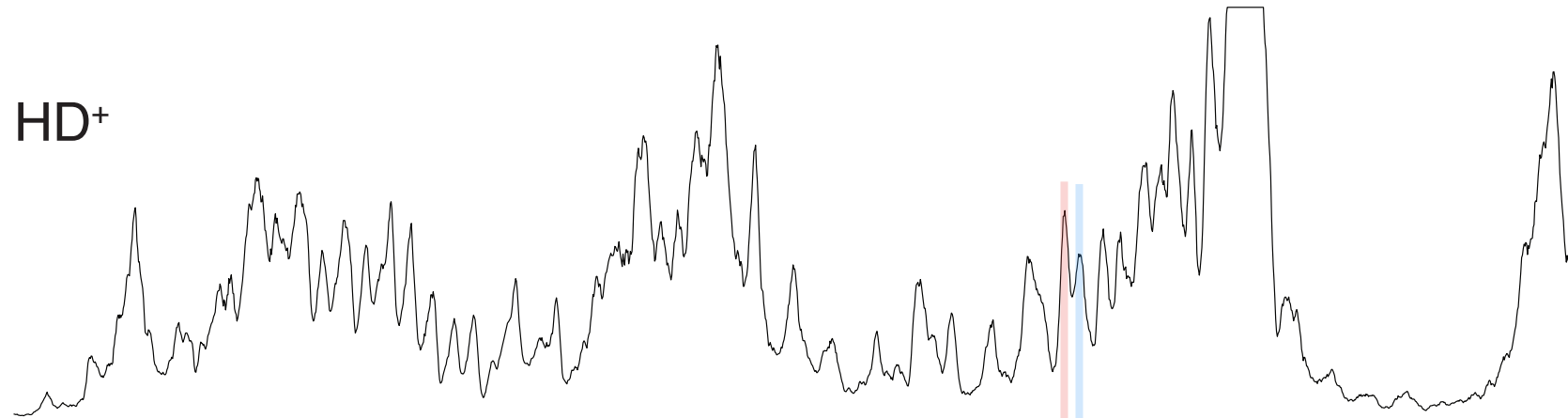
Quantum defects and H^- charge radius



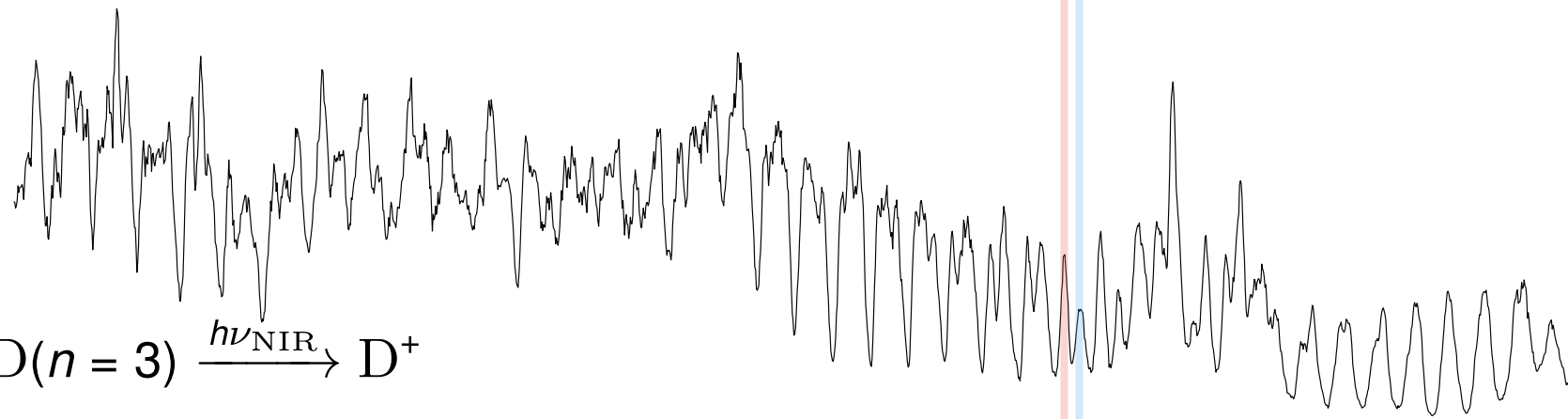
Heavy Rydberg states in HD



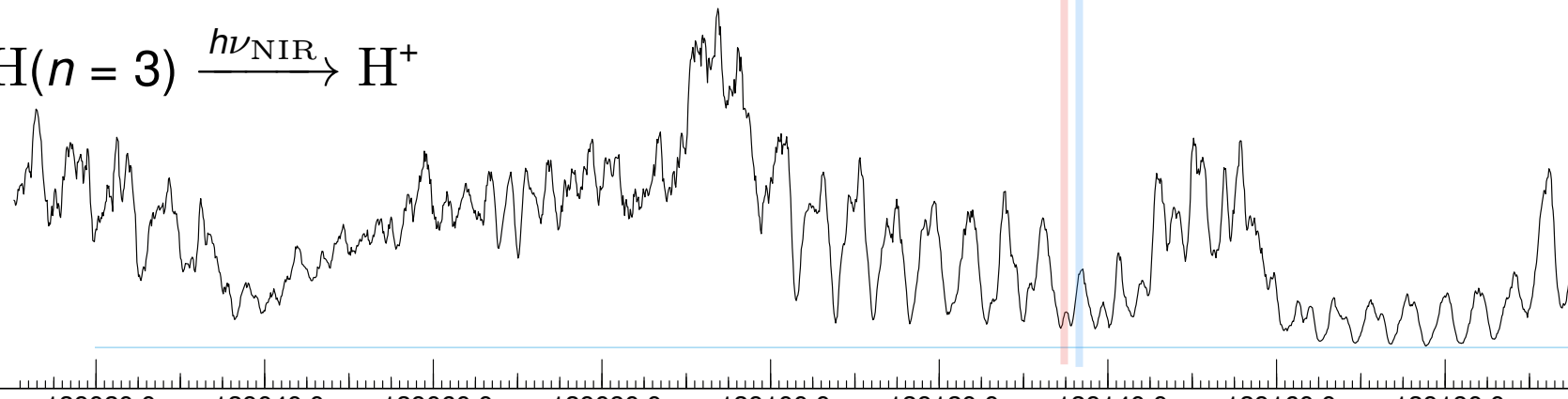
HD⁺



$D(n=3) \xrightarrow{h\nu_{\text{NIR}}} D^+$

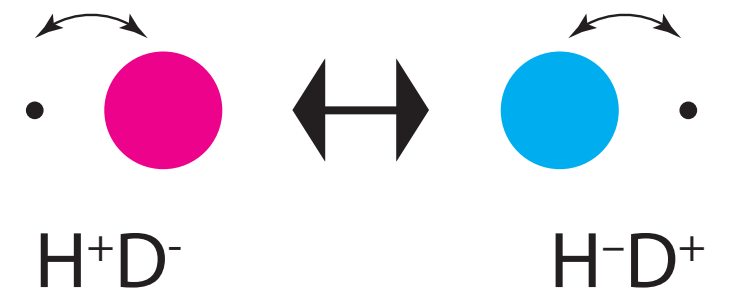
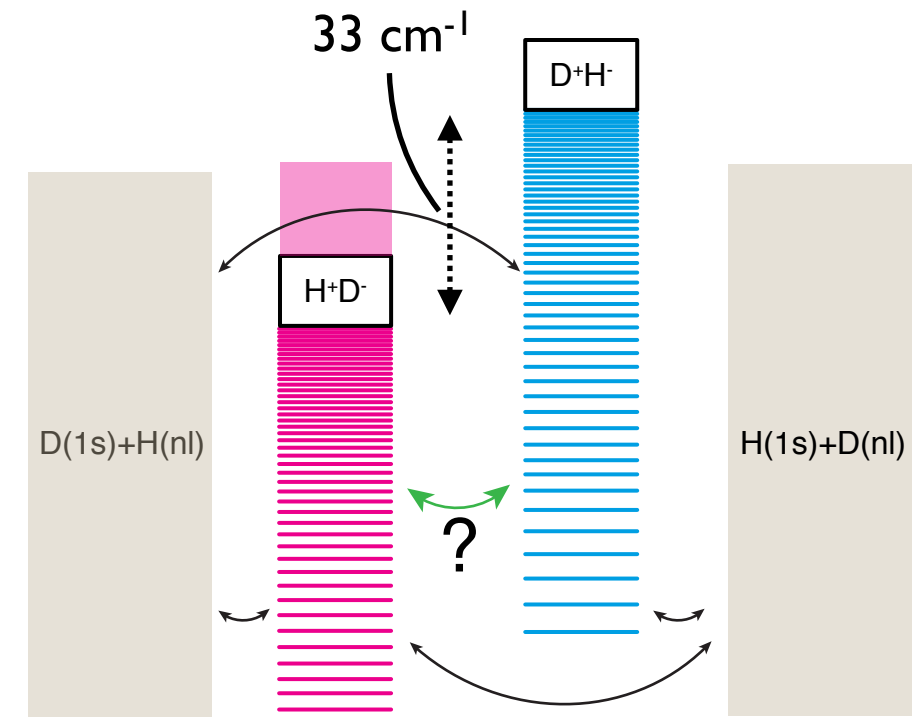


$H(n=3) \xrightarrow{h\nu_{\text{NIR}}} H^+$



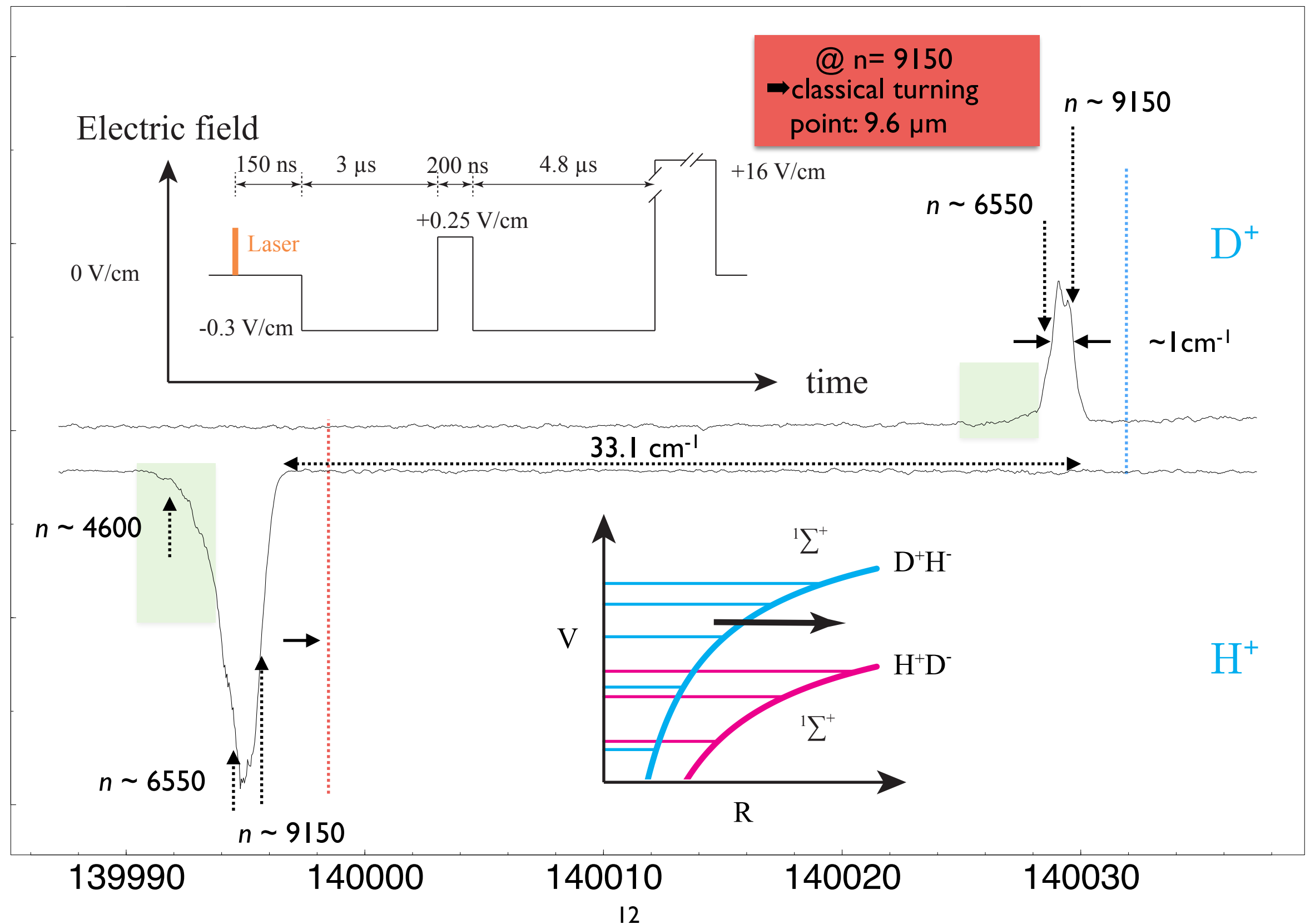
139020.0 139040.0 139060.0 139080.0 139100.0 139120.0 139140.0 139160.0 139180.0

Wave number with respect to the $X(v=0, N=0)$ ground state (cm^{-1})



Threshold ion-pair production spectroscopy (TIPPS)

using mass-analyzed threshold ionization (MATI) techniques



Conclusions & Outlook

- ➡ Observation of H^+H^- heavy Rydberg states beyond $n = 250$
- ➡ Extrapolation of the heavy Rydberg series limit (accuracy $\sim 0.23 \text{ cm}^{-1}$)
(towards improving the EA of the H atom [Lineberger: accuracy $\sim 0.15 \text{ cm}^{-1}$])
- ➡ Measurement of the H^- charge radius
- ➡ Observation of H^+D^- and H^-D^+

- ➡ Outlook:
 - Improving the EA of the D atom [Lineberger: accuracy $\sim 0.6 \text{ cm}^{-1}$]
 - Determination of the H^-/D^- charge-radius ratio
 - full analysis of the short-range dynamics (autoionization, predissociation)
combining close-coupling calculations and quantum-defect theory
 - ❖ HD: g/u-mixing nonadiabatic coupling function only calculated
for the $3 \text{ } ^1\Sigma$ states

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