H_3^+: a key molecular ion in the universe and a challenge for theorists on earth

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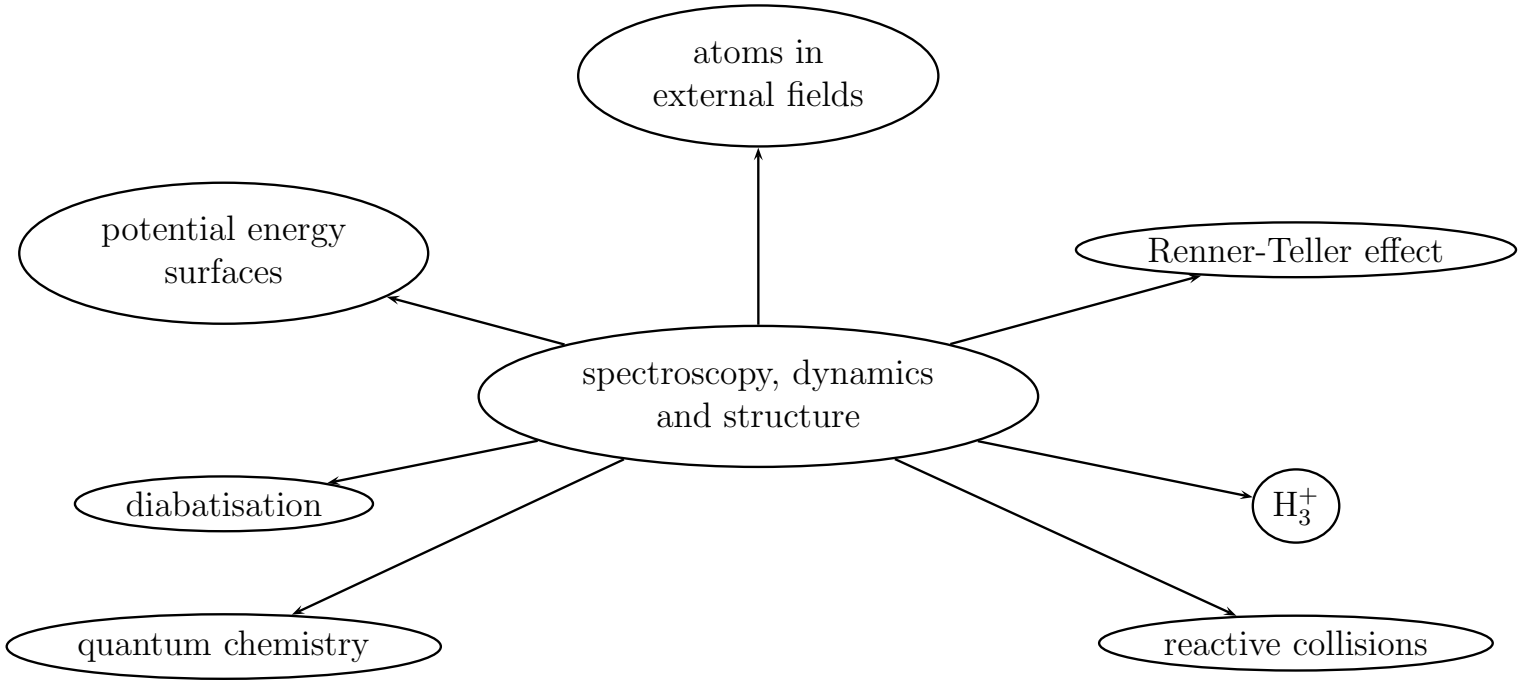
Introduction

Formation and research activities

- Student of Chemistry at Marburg and Bielefeld, Germany
- 1984, *Diplom*, thesis "The hydrogenic Stark effect"
- 1988, Doctorate, thesis "Photoionisation of hydrogen in a strong magnetic field"
- 1996, Habilitation, thesis "Dynamics and spectra of triatomic molecules with strong coupling between rotation, vibration and electronic motion"



History of H_3^+

- Discovery by J. J. Thomson, *Phil. Mag.* **21**, 225 (1911)
- Presence in plasmas, A. J. Dempster, *Phil. Mag.* **31**, 438 (1916)
- Formation via $H_2^+ + H_2 \rightleftharpoons H_3^+ + H$,
  T. R. Hogness & E. G. Lunn, *Phys. Rev.* **26**, 44 (1925)
- Prediction of D_{3h} structure, $r = 1.6\,a_0$, (modern value: $r = 1.65\,a_0$),
  C. A. Coulson, *Proc. Camb. Phil. Soc.* **31**, 244 (1935)
- Prediction of non-symmetric triangular structure,
  J. O. Hirschfelder, H. Eyring & N. Rosen, *J. Chem. Phys.* **4**, 130 (1936)
- Confirmation of D_{3h} equilibrium structure,
  H. Conroy, *J. Chem. Phys.* **40**, 603 (1964)
  R. E. Christofferson, S. Hagstrom & F. Prosser, *ibid.* **40**, 236 (1964)

Some work since the seventies

- Potential energy surface,
  G. D. Carney & R. E. Porter, *J. Chem. Phys.* **60**, 4251 (1974)
- Calculation of vibrational spectrum,
  G. D. Carney & R. E. Porter, *J. Chem. Phys.* **65**, 3547 (1976)
- Detection of H_3^+ spectrum,
  T. Oka, *Phys. Rev. Lett.* **45**, 531 (1980)
- Spectrum near dissociation,
  A. Carrington & R. A. Kennedy, *J. Chem. Phys.* **81**, 91 (1984)
- Potential energy surface and ro-vibrational calculations,
  W. Meyer, P. Botschwina & P. G. Burton,
  J. Chem. Phys. **84**, 891 (1986)
- First extensive ro-vibrational calculations,
  S. Miller & J. Tennyson, *J. Molec. Spectr.* **136**, 223 (1989)

Some recent work

- Potential energy surface with near spectroscopic accuracy,
  W. Cencek, J. Rychlewski, R. Jaquet & W. Kutzelnigg,
  J. Chem. Phys. **108**, 2831 (1997)
- Comprehensive evaluation and compilation of H_3^+ spectroscopy,
  C. M. Lindsay & B. J. McCall, *J. Molec. Spectr.* **210**, 60 (2001)
- Above barrier spectroscopy,
  J. B. Gottfried, B. J. McCall & T. Oka,
  J. Chem. Phys. **118**, 10890 (2003)
- Extended ro-vibrational calculations,
  P. Schiffels, A. Alijah & J. Hinze, *Mol. Phys.* **101**, 189 (2003)
- Vibrational states near dissociation,
  J. Tennyson, P. Barletta, J. J. Munro & B. C. Silva,
  Phil. Trans. R. Soc. A. **364**, 2903 (2006)

H_3^+: excited electronic states

- Excited electronic states, prediction of stable $^3\Sigma_u^+$,
  L. J. Schaad & W. V. Hicks, *J. Chem. Phys.* **61**, 1934 (1974)
- Triplet H_3^+ in hydrogen plasmas?
  I. McNab, *Adv. Chem. Phys.* **89**, 1 (1995)
  J. Tennyson, *Rep. Prog. Phys.* **57**, 421 (1995)
- First complete triplet potential energy surfaces and ro-vib. calculations,
  C. Sanz, O. Roncero, C. Tablero, A. Aguado & M. Paniagua,
  J. Chem. Phys. **114**, 2182 (2001)
  O. Friedrich, A. Alijah, Z. R. Xu & A. J. C. Varandas,
  Phys. Rev. Lett. **86**, 1183 (2001)
- Excited triplet states,
  L. P. Viegas, A. Alijah & A. J. C. Varandas,
  J. Phys. Chem. A **109**, 3307 (2005)
- Excited singlet states,
  L. P. Viegas, A. Alijah & A. J. C. Varandas, *J. Chem. Phys.* in press
- Electronic states in magnetic fields,
  A. V. Turbiner, N. L. Guevara & J. C. López Vieyra,
  2007, in press

Extraterrestrial H_3^+

- Detection of laboratory H_3^+ spectrum
  T. Oka, *Phys. Rev. Lett.* **45**, 531 (1980)
- First non-terrestrial spectrum: Jupiter
  L. Trafton, D. F. Lester & K. Thompson, *Astrophys. J.* **343**, L73 (1989)
  P. Drossart (and 11 others), *Nature* **340**, 539 (1989)
  Assignment to H_3^+ by J. K. G. Watson
- First spectrum from interstellar space: interstellar clouds
  T. R. Geballe & T. Oka, *Nature* **384**, 334 (1996)
- Spectrum from diffuse interstellar medium
  B. J. McCall, T. R. Geballe, K. H. Hinkle & T. Oka,
  Science **279**, 1910 (1998)
- Spectrum from the Central Molecular Zone of our galaxy, high T
  M. Goto, B. J. McCall, T. R. Geballe, T. Usuda, N. Kobayashi,
  H. Terada & T. Oka, *Publ. Astron. Soc. Jpn.* **54**, 951 (2002)
- Towards an external galaxy: extragalactic H_3^+ ?
  T. R. Geballe, M. Goto, T. Usuda, T. Oka & B. J. McCall,
  Astrophys. J. **644**, 907 (2006)
- H_3^+ on neutron stars?

Where does H_3^+ come from?

Why is there so much H_3^+?

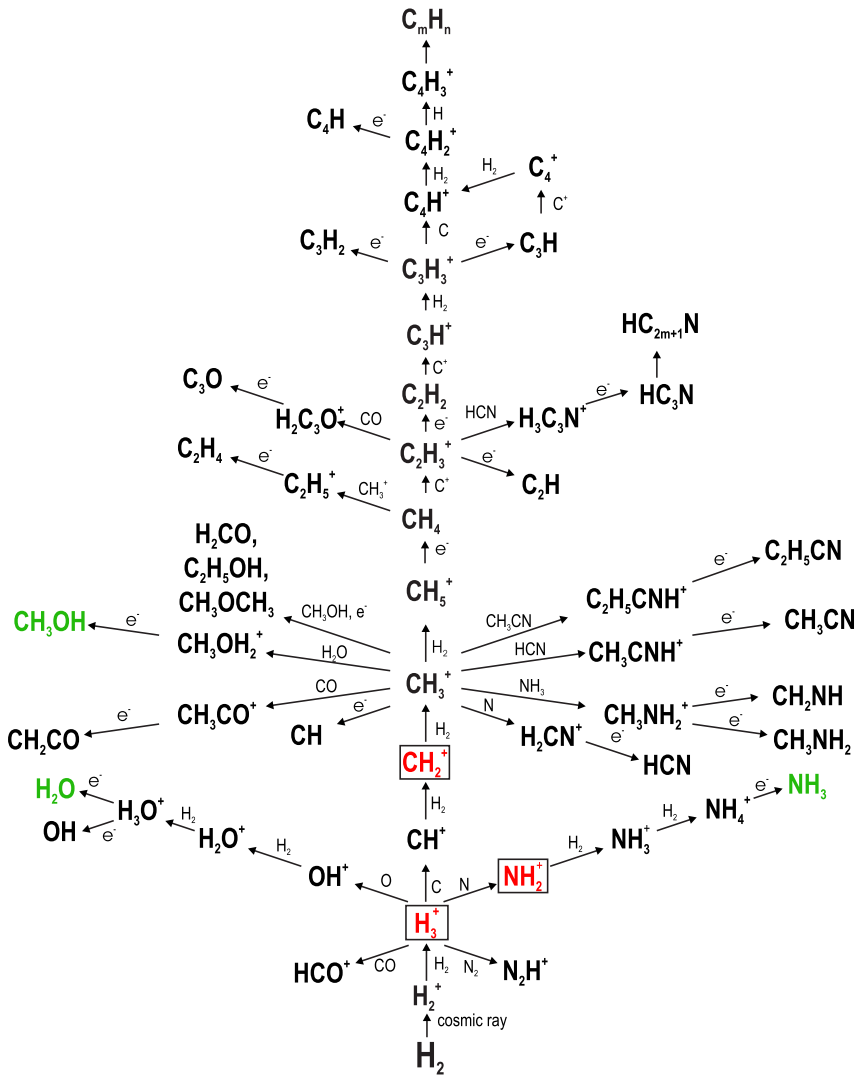
1. $H_2 \longrightarrow H_2^+ + e^-$
   $H_2^+ + H_2 \longrightarrow H_3^+ + H$

2. $H \longrightarrow H^+ + e^-$
   $H^+ + H_2(v \geq 4) \longrightarrow H_2^+ + H$
   $H_2^+ + H_2 \longrightarrow H_3^+ + H$

3. Result: $n(H_3^+) > n(H_2^+), n(H^+)$

What does it do?

Interstellar chemistry



Ultrahigh deuterium fractionation in pre-stellar cores

- Formation of deuterated species
  - $H_3^+ + HD \longrightarrow H_2D^+ + H_2$
  - $H_2D^+ + HD \longrightarrow HD_2^+ + H_2$
  - $HD_2^+ + HD \longrightarrow D_3^+ + H_2$
- Situation in extreme cases:
  $n(H_3^+) \leq n(H_2D^+) \leq n(HD_2^+) \leq n(D_3^+)$

  H. Roberts, E. Herbst & T. J. Millar, *Astrophys. J.* **591**, L41 (2003)
  C. M. Walmsley, D. R. Flower & G. P. Pineau de Forêts, *Astron. Astrophys.* **418**, 1035 (2004)

- Laboratory spectroscopy:
  T. Amano, *Phil. Trans. Roy. Soc. A* **364**, 2943 (2006)

Theory of H_3^+

H_3^+: the challenge

- H_3^+ is the most simple polyatomic
- demand for high accuracy
- test system for development of theoretical methods

- electronically simple
- light molecule, performs large amplitude vibrations

Calculation of electronic energy

H_3^+ in a singlet state:

Standard methods:

- Hartree-Fock:

$$\Phi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \alpha(1) & \alpha(2) \\ \beta(1) & \beta(2) \end{vmatrix} \varphi_1(1)\varphi_1(2)$$

- CI:

$$\Phi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \alpha(1) & \alpha(2) \\ \beta(1) & \beta(2) \end{vmatrix} \sum_{p,q} c_{pq}\varphi_p(1)\varphi_q(2);\ c_{pq} = c_{qp}$$

accuracy: $\approx 0.2\, mE_h = 50\, cm^{-1}$

Calculation of electronic energy

Specialized methods:

- CI-r12:

$$\Phi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \alpha(1) & \alpha(2) \\ \beta(1) & \beta(2) \end{vmatrix} \times \left\{ c_0 r_{12}\varphi(1,2) + \sum_{p,q} c_{pq}\varphi_p(1)\varphi_q(2);\ c_{pq} = c_{qp} \right\}$$

  Röhse, Kutzelnigg, Jaquet & Klopper, *J. Chem. Phys.* **101**, 2231 (1994)
  69 points, accuracy: $\approx 1\,\mu\mathrm{E_h} = 0.2\,\mathrm{cm}^{-1}$

- Gaussian Geminals:

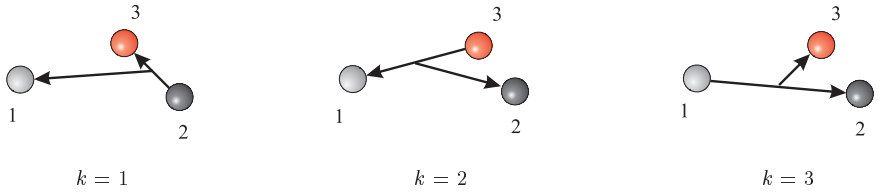
$$\Phi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \alpha(1) & \alpha(2) \\ \beta(1) & \beta(2) \end{vmatrix} \sum_n c_n \tilde{\phi}_n$$

$$\tilde{\phi}_n = (1 + P_{12}) e^{-\alpha_{1i}|\mathbf{r}_1 - A_i|^2 - \alpha_{2i}|\mathbf{r}_2 - B_i|^2 - \beta_1 r_{12}^2}$$

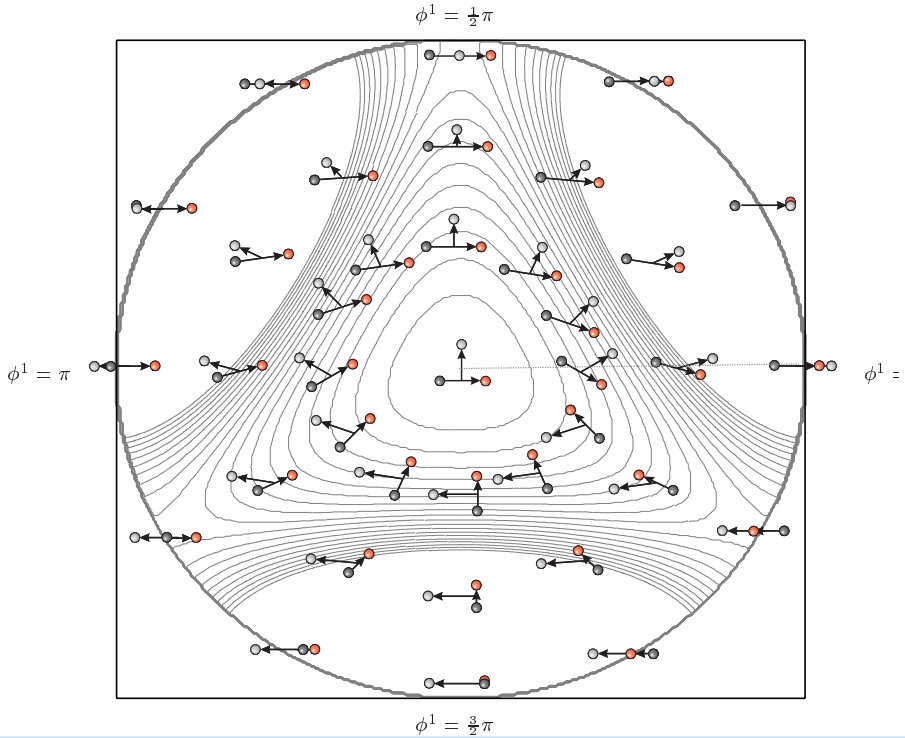
  Cencek, Rychlewski, Jaquet & Kutzelnigg, *J. Chem. Phys.* **108**, 2831 (1998)
  69 points, accuracy: $\approx 0.1\,\mu\mathrm{E_h} = 0.02\,\mathrm{cm}^{-1}$

Coordinate systems for triatomic molecules

- Jacobi coordinates: $\mathbf{r}_k, \mathbf{R}_k$



- Hyperspherical coordinates:
  internal coordinates: ρ, θ, ϕ , Euler angles: α, β, γ



Hyperspherical method: harmonics

Three-particle case:

$$T(\rho,\Omega) = -\frac{1}{2\mu\rho^5}\frac{\partial}{\partial\rho}\rho^5\frac{\partial}{\partial\rho} + \frac{\Lambda^2(\Omega)}{2\mu\rho^2}$$

$\Omega = \alpha, \beta, \gamma, \theta, \phi$

Hyperspherical harmonics:

$$\Lambda^2(\Omega)\Psi^{JM}_{K\nu s}(\Omega) = K(K+4)\Psi^{JM}_{K\nu s}(\Omega)$$

$$-i\frac{\partial}{\partial\phi}\Psi^{JM}_{K\nu s}(\Omega) = \frac{\nu}{2}\Psi^{JM}_{K\nu s}(\Omega)$$

L. Wolniewicz, *J. Chem. Phys.* **90**, 371 (1988)

Two-particle case:

$$T(r,\theta,\phi) = -\frac{1}{2\mu r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{l^2(\theta,\phi)}{2\mu r^2}$$

Spherical harmonics:

$$l^2(\theta,\phi)Y_{lm}(\theta,\phi) = l(l+1)Y_{lm}(\theta,\phi)$$

$$-i\frac{\partial}{\partial\phi}Y_{lm}(\theta,\phi) = mY_{lm}(\theta,\phi)$$

Hyperspherical method: Schrödinger equation

Schrödinger equation:

$$\{T(\rho,\Omega)+V(\rho,\theta,\phi)-E_k\}\,\Phi_k(\rho,\Omega)=0$$

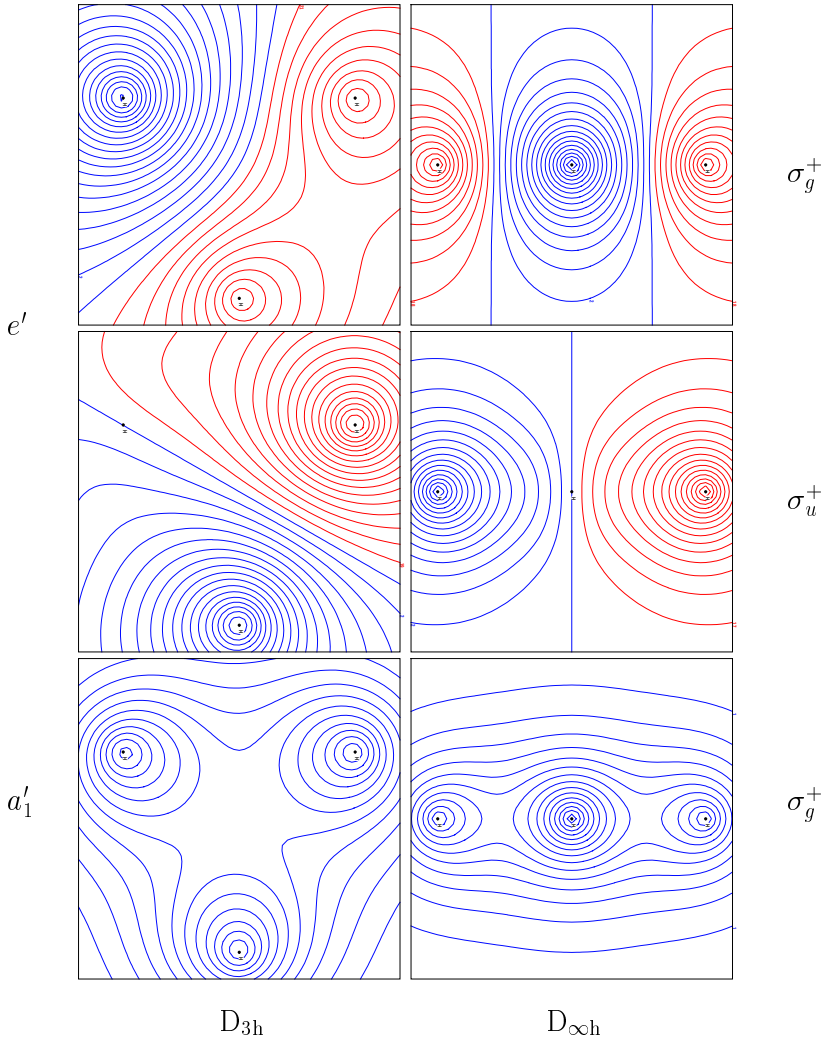
Expansion of wave function:

$$\Phi_k(\rho,\Omega)=\sum_{i=(K\nu s)\in\Gamma}\Psi_i(\Omega)\frac{R_{ik}(\rho)}{\rho^{5/2}}$$

System of radial equations:

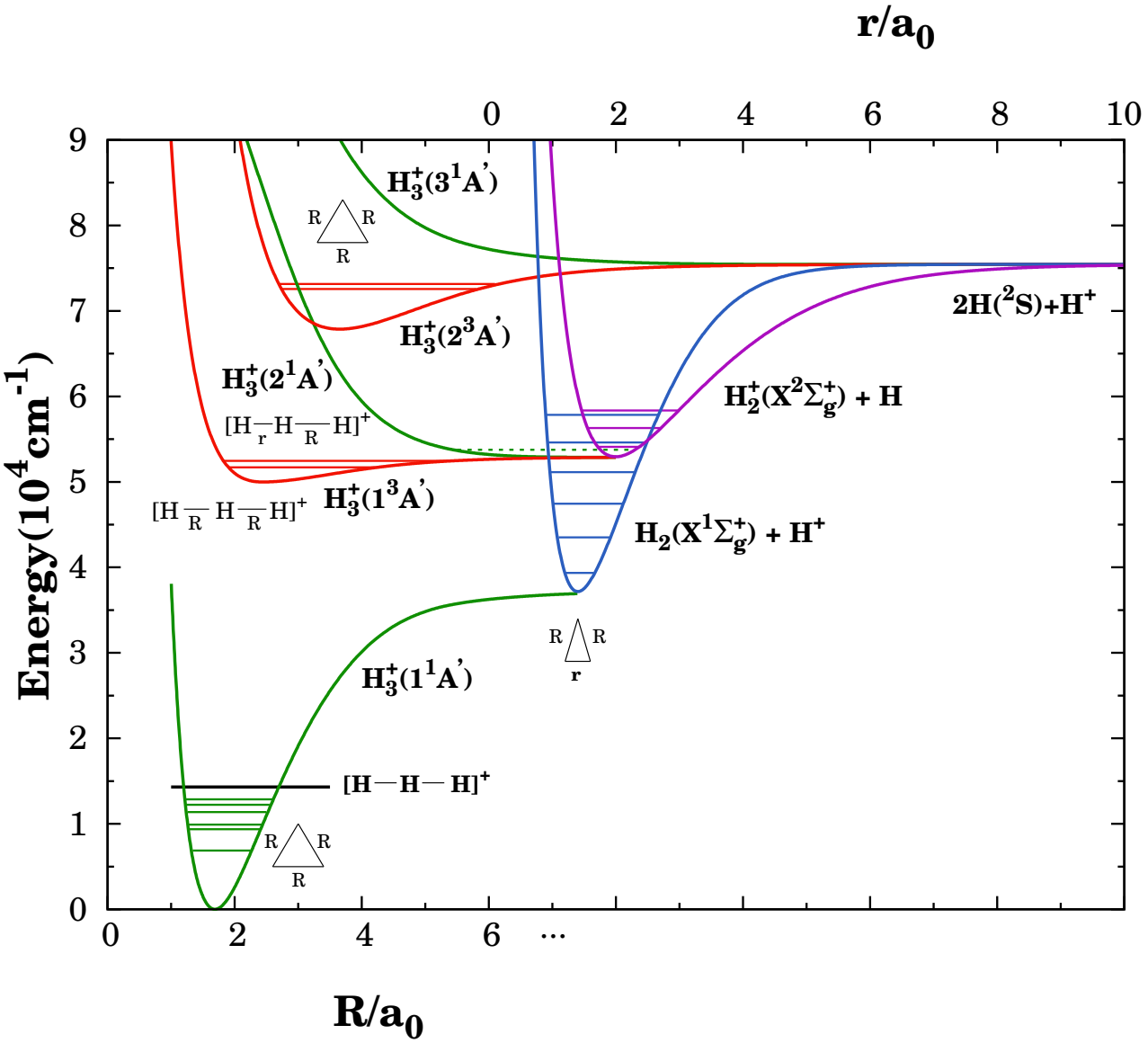
$$\sum_i\left\{\left(-\frac{1}{2\mu\rho^2}\frac{\partial^2}{\partial\rho^2}+\frac{K(K+4)+\frac{15}{4}}{2\mu\rho^2}-E_k\right)\delta_{ij}+\langle\Psi_i|V(\rho,\theta,\phi)|\Psi_j\rangle\right\}R_{jk}(\rho)=0$$

H_3^+: Molecular orbitals and electronic states



config.	states	
	D_{3h}	others
${a_1'}^2$	$X\,^1A_1'$	
$a_1'e'$	$a\,^3E'$	$\rightarrow a\,^3\Sigma_u^+$ & $2\,^3A'$
	$A\,^1E'$	$\rightarrow A\,^1\Sigma^+$ & $3\,^1A'$

H_3^+: Cuts through potential energy surfaces

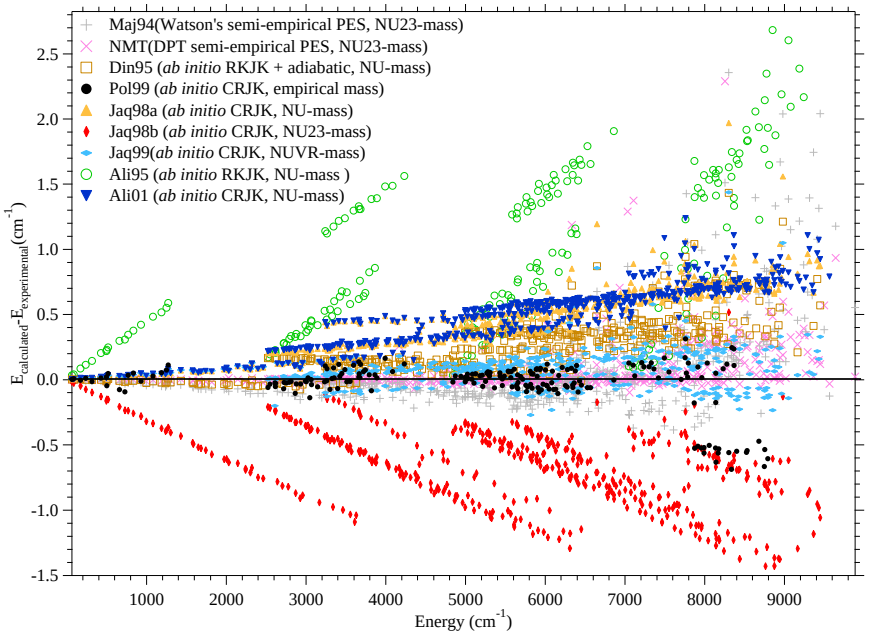


Electronic singlet state

Results H_3^+ ($X\,^1A_1'$): CRJK surface

Schiffels, Alijah & Hinze, *Molec. Phys.* **101**, 175 (2003), *ibid.*, **101**, 189 (2003)

Ro-vibrational states:
Comparison between theoretical and experimental results



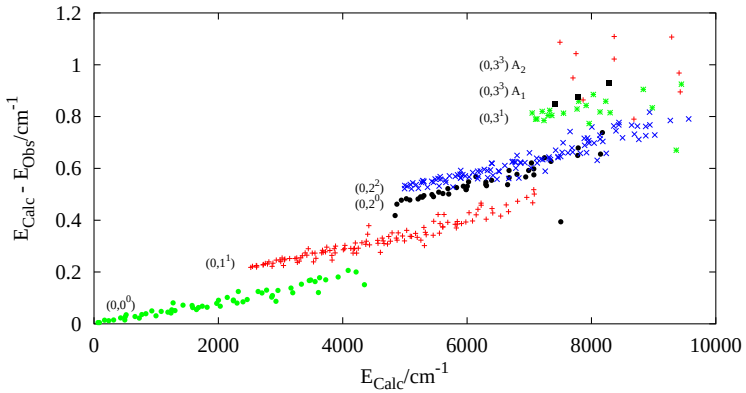
(from M. Lindsay & B.J. McCall, *J. Mol. Spectrosc.* **210**, 60 (2001))

Our "blue" results:

- accuracy of potential energy surface: $\sim 10^{-7}\,E_h = 0.02\,cm^{-1}$ Cencek *et. al.*, *J. Chem. Phys.* **108**, 2831 (1998)
- diagonal adiabatic and relativistic corrections included
- Errors of theoretical results: $\leq 1\,cm^{-1}$. Why?

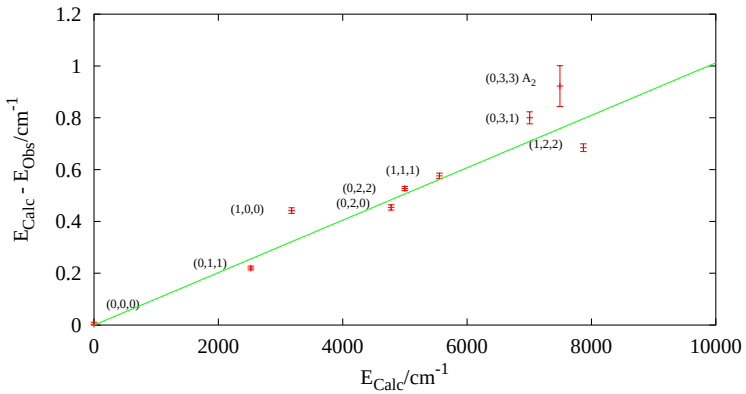
Schiffels, Alijah & Hinze, *Molec. Phys.* **101**, 175 (2003), *ibid.* **101**, 189 (2003)

- Determination of parameters



$$\begin{aligned} \Delta E &= E_{calc} - E_{obs} \\ &= a_0 + a_1\, J(J+1) + a_2\, G^2 \\ E^{(1)}_{corr} &= E_{calc} - a_0 - a_1\, J(J+1) - a_2\, G^2 \end{aligned}$$

- Extrapolation



$$\begin{aligned} a_0 &= b_1\, E^0_{calc} \\ E^{(2)}_{corr} &= E_{calc} - b_1 E^0_{calc} \\ &\quad -\bar{a}_1\, J(J+1) - \bar{a}_2\, G^2 \\ E^{(4)}_{corr} &= E_{calc} - b_1 E_{calc} \end{aligned}$$

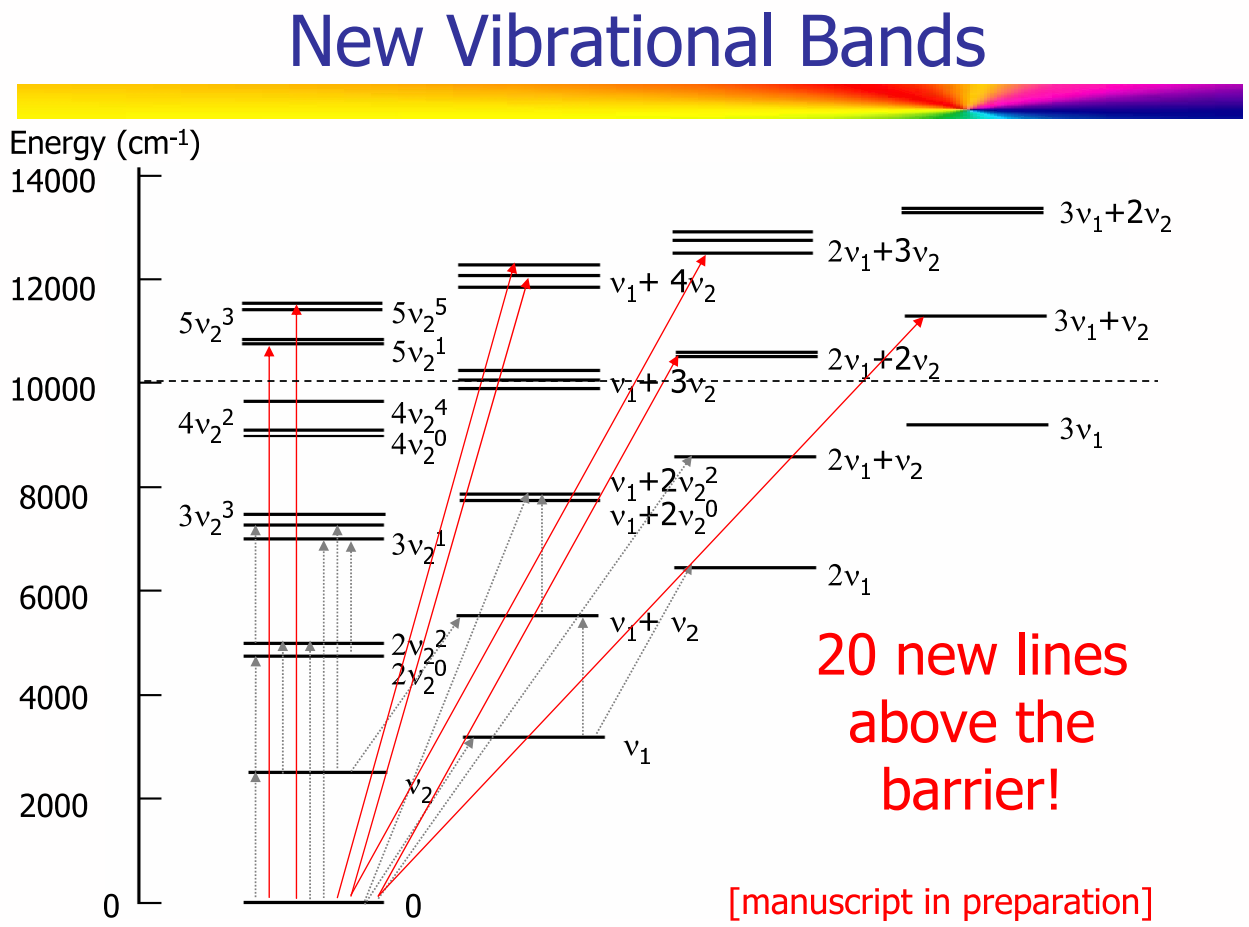
Above barrier calculations

A. Alijah, work in progress

Calculations above barrier to linearity, i.e. $E > 10000\,\mathrm{cm}^{-1}$:

- to assist ongoing experimental work by the Oka group (Chicago)
- hyperspherical method well suited
- extrapolated off-diagonal adiabatic corrections included
- spectroscopic assignments

from J. Gottfried, Oka group (Chicago)



Predictions for highly excited states

J. Gottfried, *Phil. Trans. R. Soc. A*, **364**, 2917 (2006)

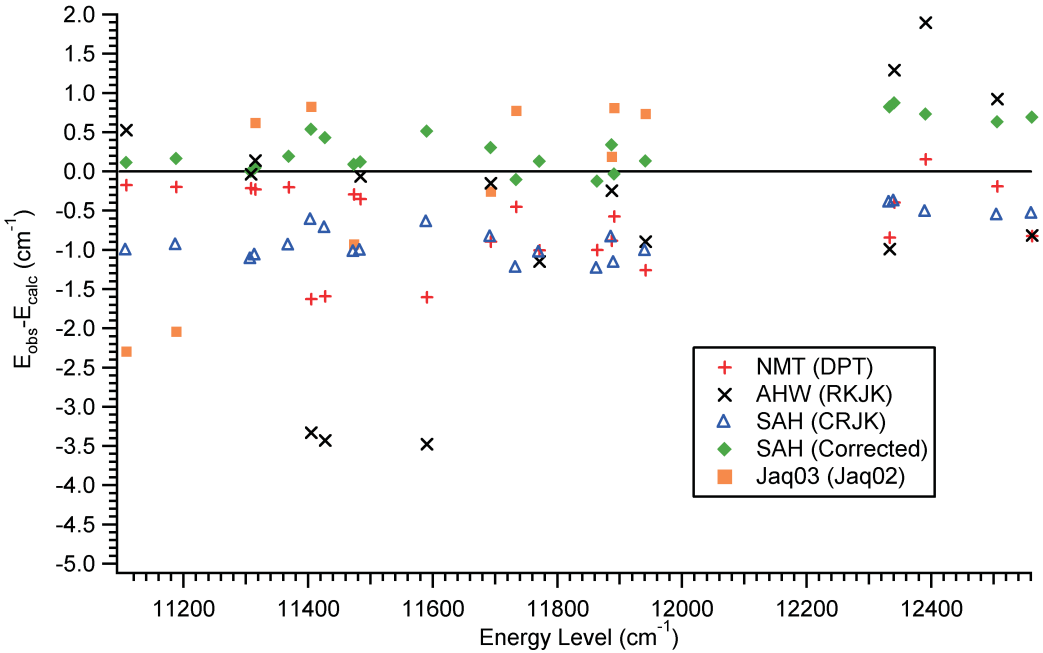


Figure 3.7: Observed minus calculated energy levels for H_3^+ (see Table 3.6 for references). The empirically corrected calculations of SAH most accurately match the experimental data, although their deviation from the observed values increases at higher energies.

- most accurate predictions
- non-adiabatic effects over-estimated at high energies

Singlet states of H_3^+: DIM representation

Viegas, Alijah & Varandas, *J. Chem. Phys.* (2007)

- Method: Diatomics In Molecules, DIM (Ellison, 1963)
  no three-body interactions in the Hamiltonian!

$$\mathbf{H} = \begin{pmatrix} E(1)+\epsilon(2,3) & \Delta(3) & \Delta(2) \\ \Delta(3) & E(2)+\epsilon(3,1) & \Delta(1) \\ \Delta(2) & \Delta(1) & E(3)+\epsilon(1,2) \end{pmatrix}$$

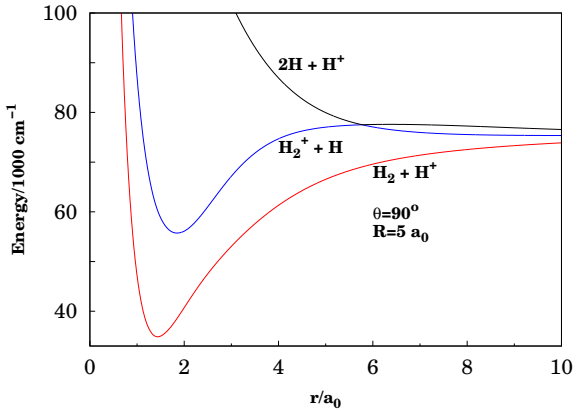
$$\begin{aligned} E(i) &= V^{(2)}_{[H_2,X]}(R_i) \\ \epsilon(j,k) &= \frac{1}{2}\left[V^{(2)}_{[H_2^+,X]}(R_j) + V^{(2)}_{[H_2^+,A]}(R_j) + V^{(2)}_{[H_2^+,X]}(R_k) + V^{(2)}_{[H_2^+,A]}(R_k)\right] - 2E_H \\ \Delta(k) &= \frac{1}{2}\left[V^{(2)}_{[H_2^+,X]}(R_k) - V^{(2)}_{[H_2^+,A]}(R_k)\right] \end{aligned}$$

- Inclusion of three-body terms respecting permutational symmetry:
  $|\mathbf{H} - \lambda\mathbf{I}| = |\mathbf{P_{ij}H} - \lambda\mathbf{I}|$

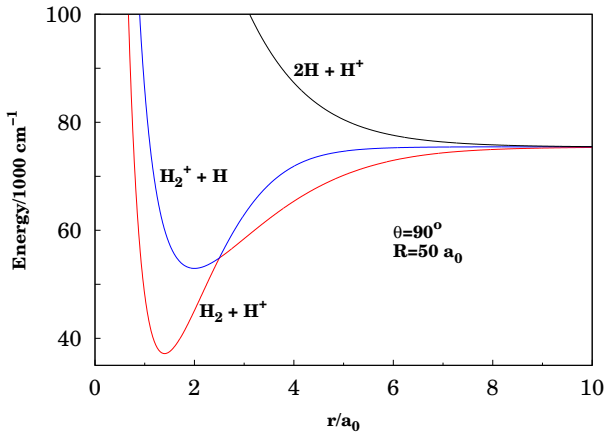
$$H_{ii} \rightarrow H_{ii} + V^{(3)}(\mathbf{R}) \,, \qquad H_{ij} \rightarrow H_{ij} - \left[\tilde{V}^{(3)}(\mathbf{R})\right]^2$$

Singlet states of H_3^+

- Conical intersection ($A\,^1\Sigma^+$ / $3\,^1A'$)



- Avoided crossing ($X\,^1A_1'$ / $A\,^1\Sigma^+$)



charge transfer $H_2 + H^+ \rightleftharpoons H_2^+ + H$: a non-adiabatic process

Singlet states of H_3^+

- $3^1A'$:
  - dissociation channel: $2H\,(^2S) + H^+$, $-1.0000\,E_h$
  - energy minimum: $-1.000097\,E_h$, $21.36\,cm^{-1}$ below dissociation
  - D_{3h} configuration, $r = 11.49\,a_0$
- $2^1A'$:
  - dissociation channel: $H_2^+\,(X^2\Sigma_g^+) + H\,(^2S)$, $-1.1026\,E_h$
  - energy minimum: $-1.102894\,E_h$, $57.07\,cm^{-1}$ below dissociation
  - $C_{\infty v}$ configuration, $r_1 = 1.99\,a_0$, $r_2 = 7.54\,a_0$, $r_3 = 9.53\,a_0$
  - supports one D_3^+ vibrational state
- $1^1A'$:
  - dissociation channel: $H_2\,(X^1\Sigma_g^+) + H^+$), $-1.174475\,E_h$
  - energy minimum: $-1.343833\,E_h$, $37169.71\,cm^{-1}$ below dissociation
  - D_{3h} configuration, $r = 1.65\,a_0$

Electronic triplet state

Triplet H_3^+: motivation

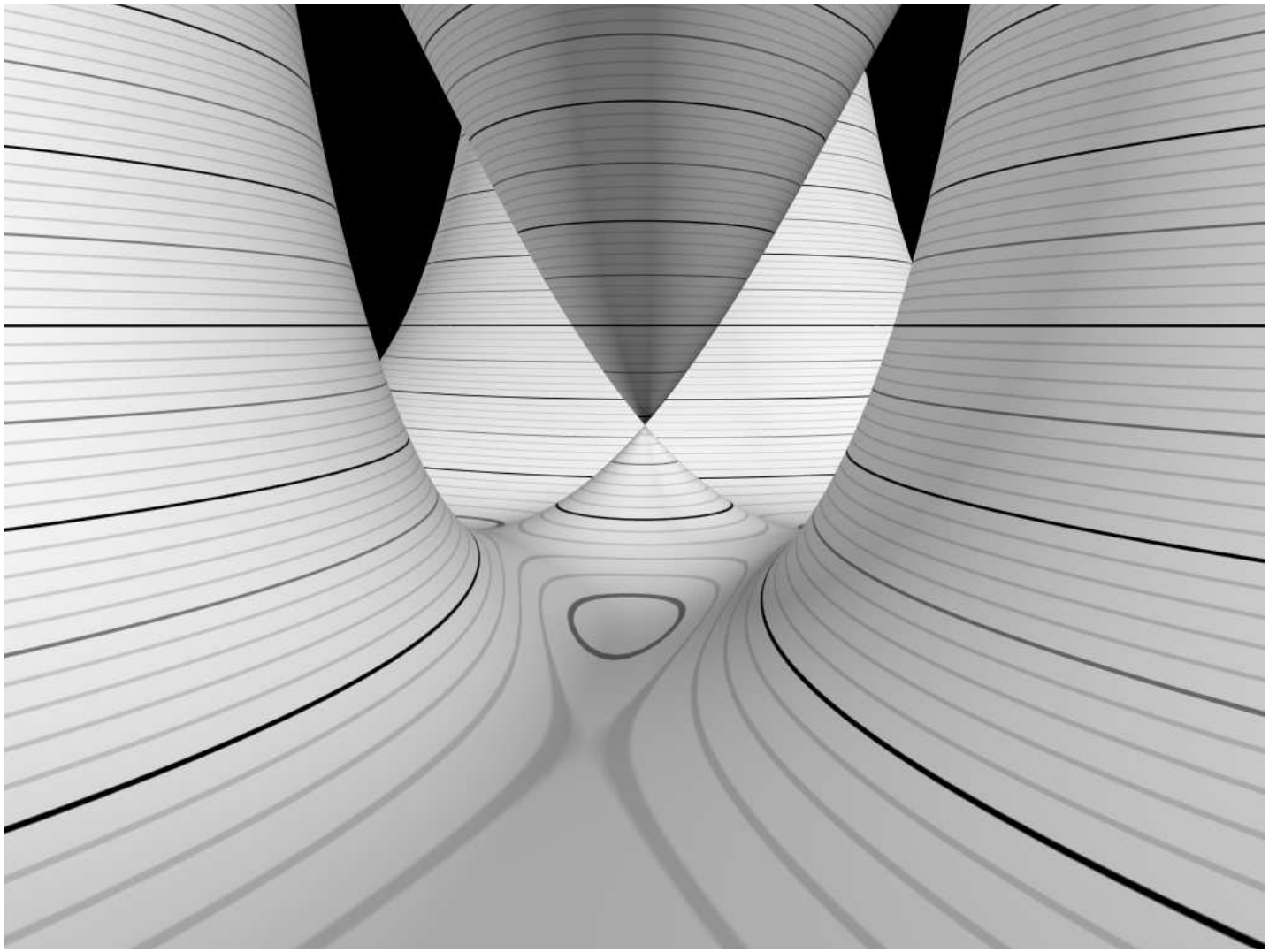
- "No accurate calculations of vibration-rotation levels ... have been published, and no spectroscopic observations have been reported, which involve the $^3\Sigma_u^+$ state. Such calculation and observations would be extremely interesting."
  I. McNab, *Adv. Chem. Phys.* **89**, 1 (1995)
- "It is possible that amongst the many H_3^+ lines that have been observed in hydrogen plasmas, some will belong to the $^3\Sigma_u^+$ state of H_3^+. But in the absence of a full potential energy surface for this state and sophisticated ro-vibrational calculations, these transitions will remain among the many that have yet to be assigned."
  J. Tennyson, *Rep. Prog. Phys.* **57**, 421 (1995)

Triplet H_3^+: formation

Triplet H_3^+ may be formed by electron impact excitation

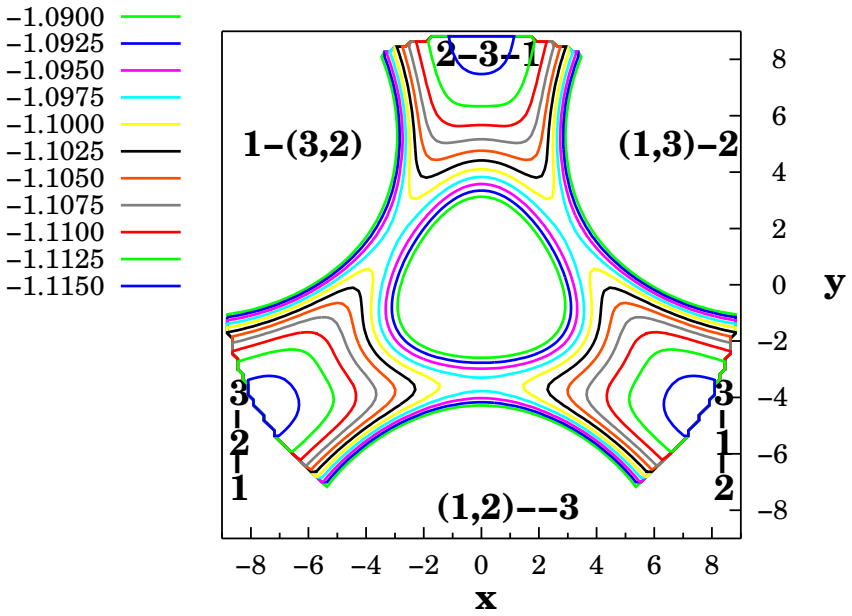
$$H_3^+(X\,^1A_1') \xrightarrow{e^-} H_3^+(a\,^3\Sigma_u^+)$$

Lowest triplet states of H_3^+: view of surfaces



H_3^+: Characterisation of the $^3E'$ surface

- upper sheet:
  dissociation channel: $2H\,(^2S)\ +\ H^+$, $-1.0000\,E_h$
  energy minimum: (D_{3h}): $-1.034590\,E_h$, $r = 3.610\,a_0$
- lower sheet:
  dissociation channel: $H_2^+\,(^2\Sigma_g^+)\ +\ H\,(^2S)$, $-1.1026\,E_h$
  energy minimum: $(D_{\infty h})$: $-1.11610627\,E_h$, $r = 2.454\,a_0$

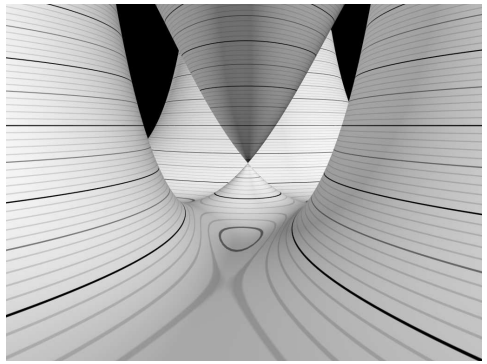


depth: $2947\,cm^{-1}$
barrier height: $2598\,cm^{-1}$

van der Waals complex

Global representation of the $^3E'$ surface

Cernei, Alijah & Varandas, *J. Chem. Phys.* **118**, 2637 (2003)
Viegas, Cernei, Alijah & Varandas, *J. Chem. Phys.* **120**, 253 (2004)
Varandas, Alijah & Cernei, *Chem. Phys.* **308**, 285 (2005)



Double many-body expansion (DMBE), Varandas (1988)

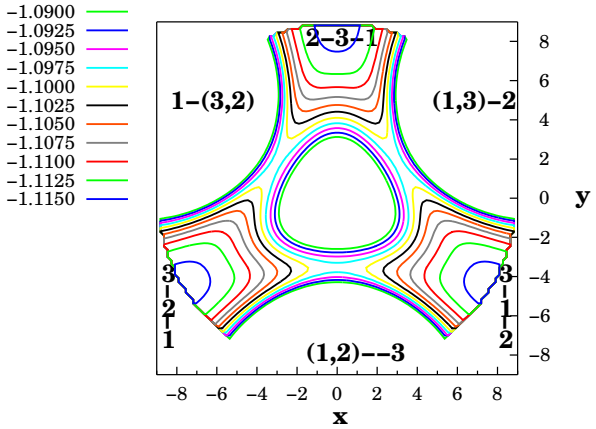
$$V_{u/l}(\mathbf{R}) = \sum_i V^{(1)} + \sum_i V^{(2)}_{u/l}(R_i) + V^{(3)}_{u/l}(\mathbf{R})$$

Special form of three-body term: (Γ_2 Jahn-Teller coordinate)

$$V^{(3)}_{u/l}(\mathbf{R}) = P_1(\mathbf{R}) \pm \Gamma_2 P_2(\mathbf{R})$$

Delocalized ro-vibrational states

Friedrich, Alijah, Xu & Varandas, *Phys. Rev. Lett.* **86**, 1183 (2001)
Alijah, Viegas, Cernei & Varandas, *J. Mol. Spectrosc.* **221**, 163 (2003)
H_2D^+: Alijah & Varandas, *J. Phys. Chem. A* **110**, 110 (2006)

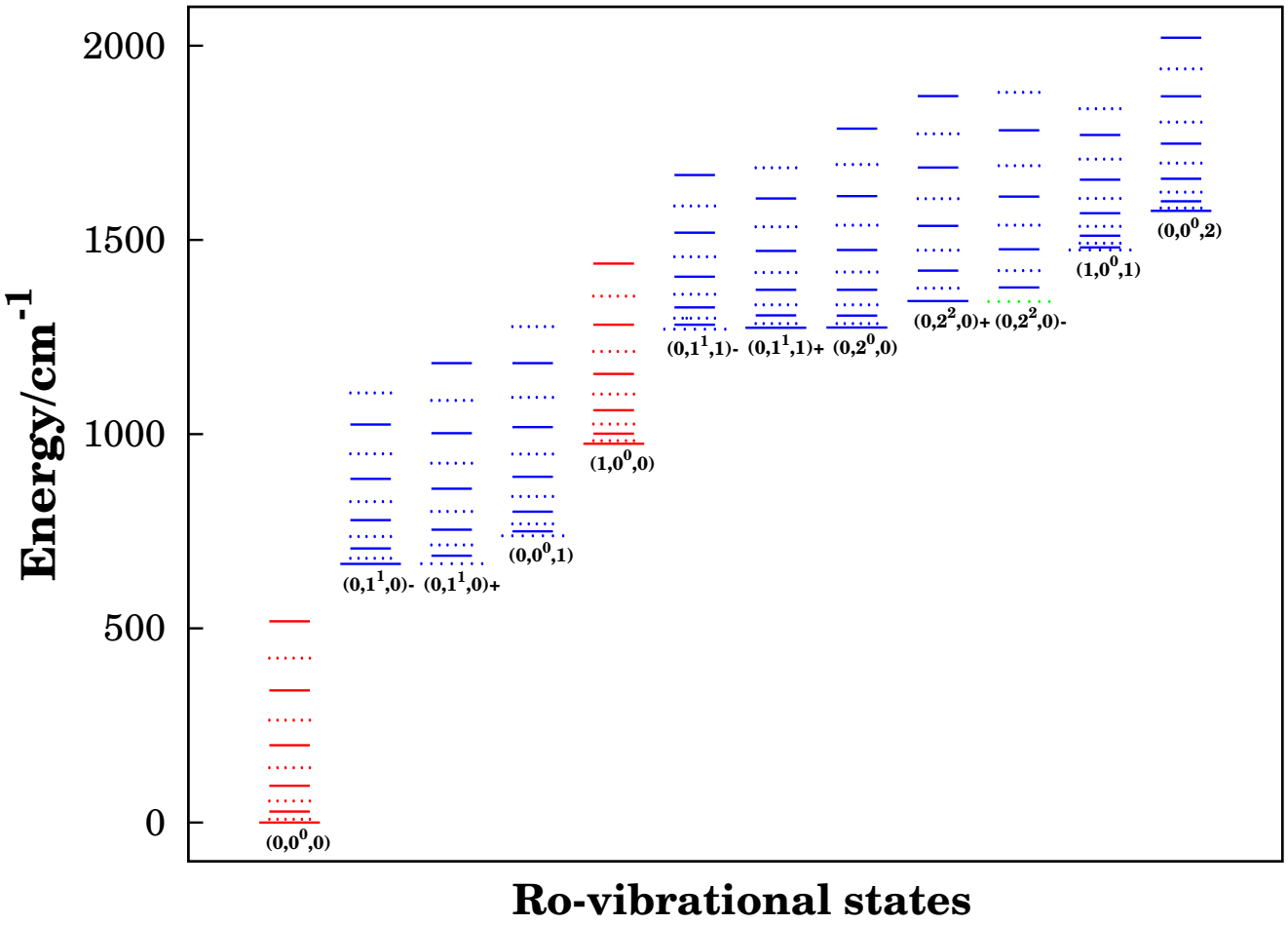


$$
\begin{aligned}
|\Psi_A^{\pm}\rangle &\sim |\Psi_I^{\pm}\rangle + |\Psi_{II}^{\pm}\rangle + |\Psi_{III}^{\pm}\rangle \\
|\Psi_{E,\xi}^{\pm}\rangle &\sim |\Psi_I^{\pm}\rangle + \omega\,|\Psi_{II}^{\pm}\rangle + \omega^2|\Psi_{III}^{\pm}\rangle \\
|\Psi_{E,\eta}^{\pm}\rangle &\sim |\Psi_I^{\pm}\rangle + \omega^2|\Psi_{II}^{\pm}\rangle + \omega\,|\Psi_{III}^{\pm}\rangle \quad ; \qquad \omega = e^{\frac{2\,\pi\,i}{3}}
\end{aligned}
$$

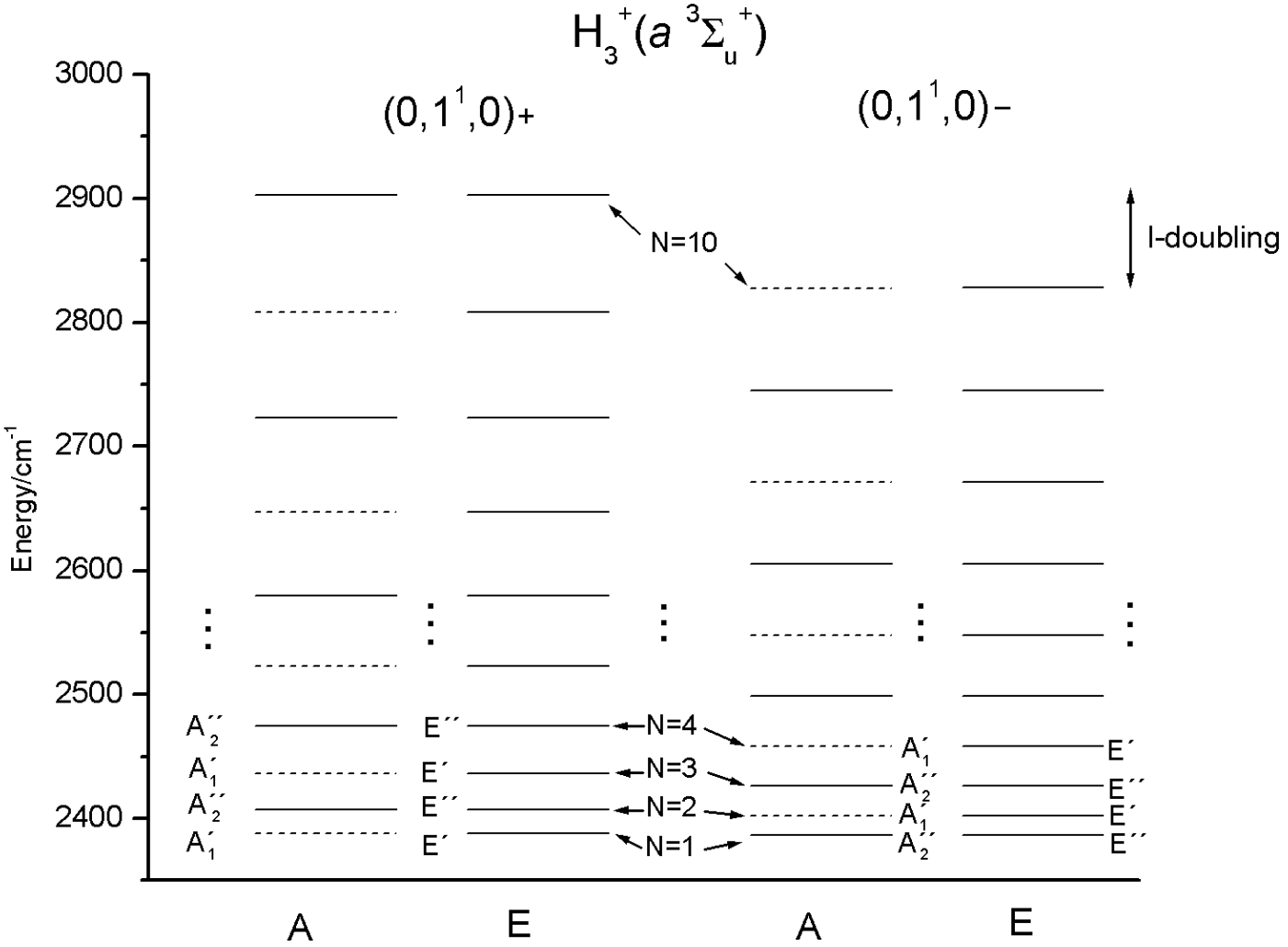
$$
|\Psi^{\pm}\rangle = \frac{1}{\sqrt{2}}|v_1 v_2^{|\ell|} v_3\rangle\ \left(|N\ell\rangle \pm |N-\ell\rangle\right)
$$

Vibrational structure

Alijah, Viegas, Cernei & Varandas, *J. Mol. Spectrosc.* **221**, 163 (2003)
560 ro-vibrational states identified ($J \leq 10$)



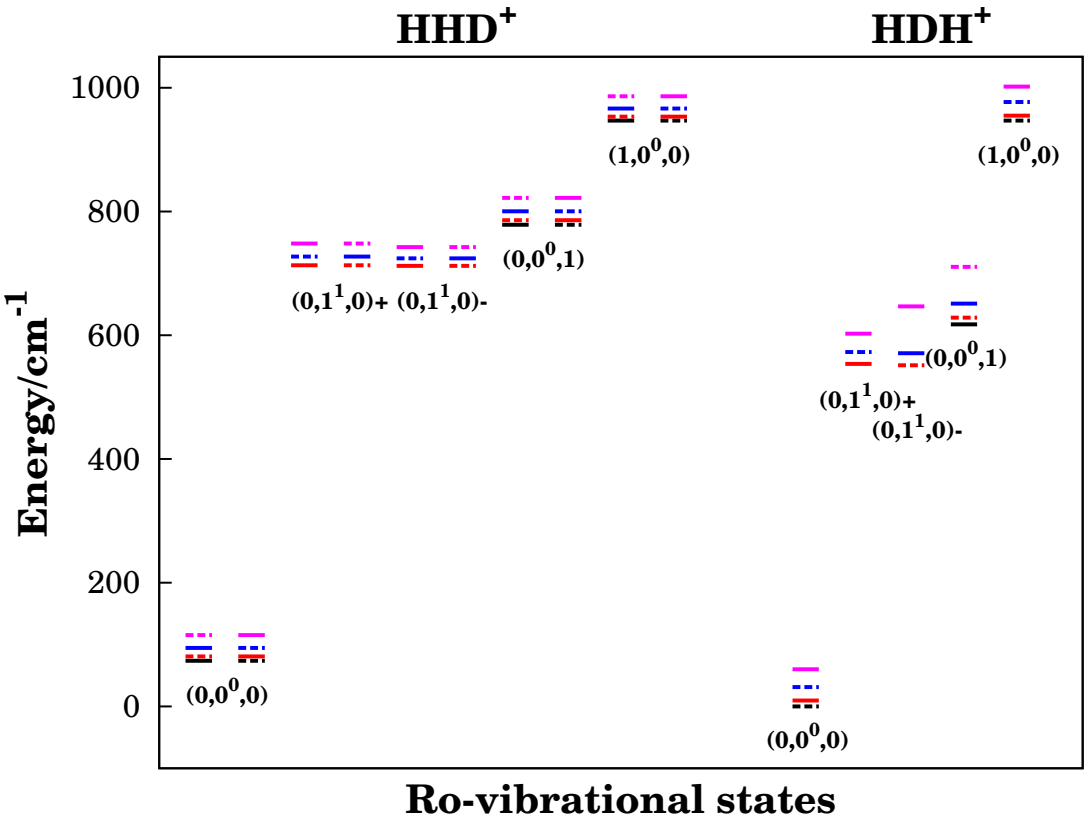
Rotational structure



H_2D^+: ro-vibrational structure

Alijah & Varandas, *J. Phys. Chem. A* **110**, 5499 (2006)

Isomers: HDH^+
HHD^+ ($H_{[1]}H_{[2]}D^+$ and $H_{[2]}H_{[1]}D^+$)



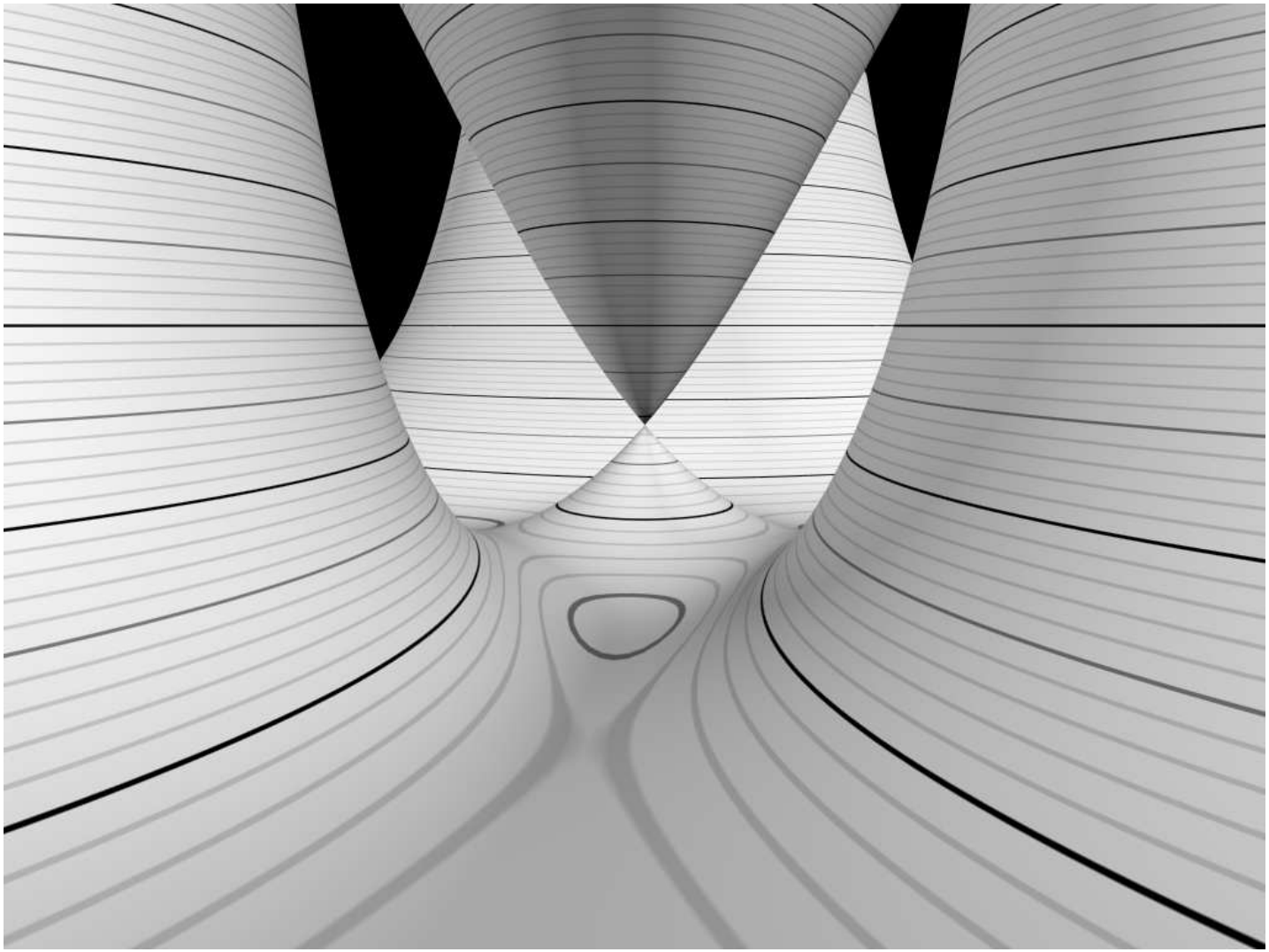
Transition frequencies: (far IR)

molecule	initial state	Γ_{rve}(w)	final state	Γ_{rve}(w)	ω/cm^{-1}
H_3^+	$N=0,\ (0,0^0,0)$	$A_2'(4)$	$N=1,\ (0,1^1,0)-$	$A_2''(4)$	665.89
		$E'(2)$	$N=1,\ (0,1^1,0)-$	$E''(2)$	665.89
H_3^+	$N=0,\ (0,0^0,0)$	$A_2'(4)$	$N=1,\ (0,0^0,1)$	$A_2''(4)$	749.71
		$E'(2)$	$N=1,\ (0,0^0,1)$	$E''(2)$	749.72
H_3^+	$N=0,\ (0,0^0,0)$	$E'(2)$	$N=1,\ (1,0^0,0)$	$E''(2)$	984.12
HDH^+	$N=0,\ (0,0^0,0)$	$B_2(3)$	$N=1,\ (0,1^1,0)-$	$B_1(3)$	551.46
HDH^+	$N=0,\ (0,0^0,0)$	$B_2(3)$	$N=1,\ (0,0^0,1)$	$B_1(3)$	628.32
HHD^+	$N=0,\ (0,0^0,0)$	$A_1(1)$	$N=1,\ (0,1^1,0)-$	$A_2(1)$	638.23
		$B_2(3)$	$N=1,\ (0,1^1,0)-$	$B_1(3)$	638.23
HHD^+	$N=0,\ (0,0^0,0)$	$A_1(1)$	$N=1,\ (0,0^0,1)$	$A_2(1)$	712.13
		$B_2(3)$	$N=1,\ (0,0^0,1)$	$B_1(3)$	712.13
HHD^+	$N=0,\ (0,0^0,0)$	$A_1(1)$	$N=1,\ (1,0^0,0)$	$A_2(1)$	879.64
		$B_2(3)$	$N=1,\ (1,0^0,0)$	$B_1(3)$	879.64

Selection rules:

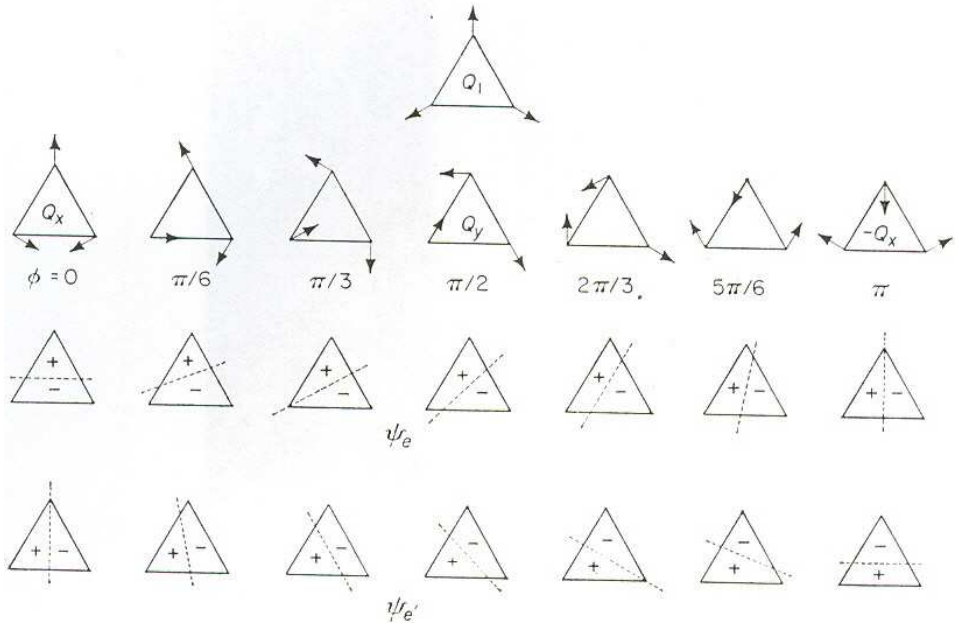
H_3^+, D_3^+	$\Delta J = 0, \pm 1$	$A_1' \leftrightarrow A_1''$, $A_2' \leftrightarrow A_2''$, $E' \leftrightarrow E''$
H_2D^+, D_2H^+	$\Delta J = 0, \pm 1$	$A_1 \leftrightarrow A_2$, $B_1 \leftrightarrow B_2$

Upper sheet: $2\,^3A'$



Geometrical or Berry phase

Longuet-Higgins, *Adv. Spectrosc.* **2**, 429 (1961)



- adiabatic electronic wave functions φ:

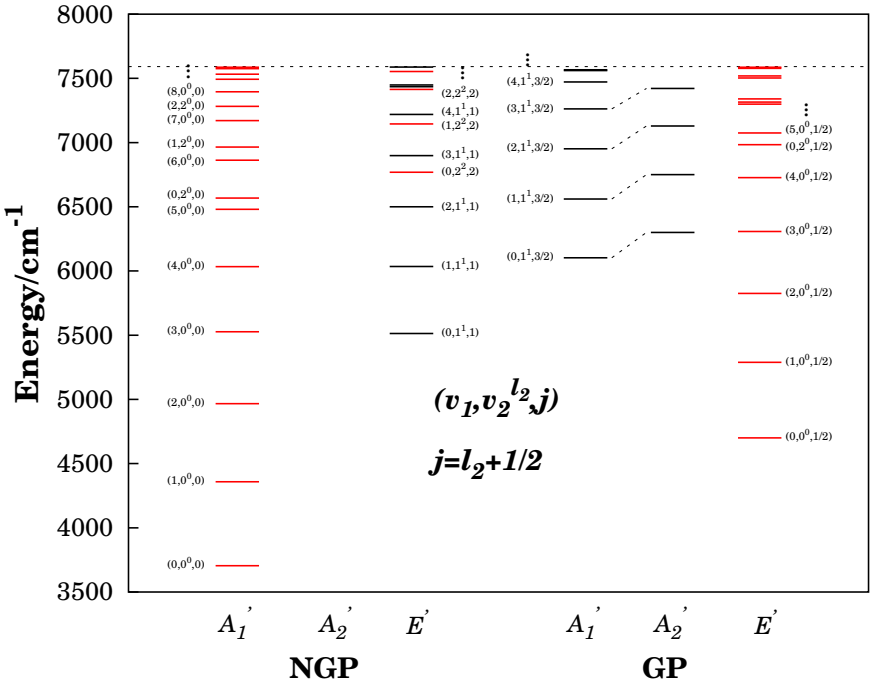
$$\oint_0^{2\pi} d\phi\, \varphi(Q_1, Q_2, \phi; \mathbf{r}) = \pi$$

- boundary conditions for rovibrational wave functions Θ:

$$\Theta(Q_1, Q_2, \phi = 0) = -\Theta(Q_1, Q_2, \phi = 2\pi)$$

Słonczewski resonances

Viegas, Alijah & Varandas, *J. Phys. Chem. A* **109**, 3307 (2005)

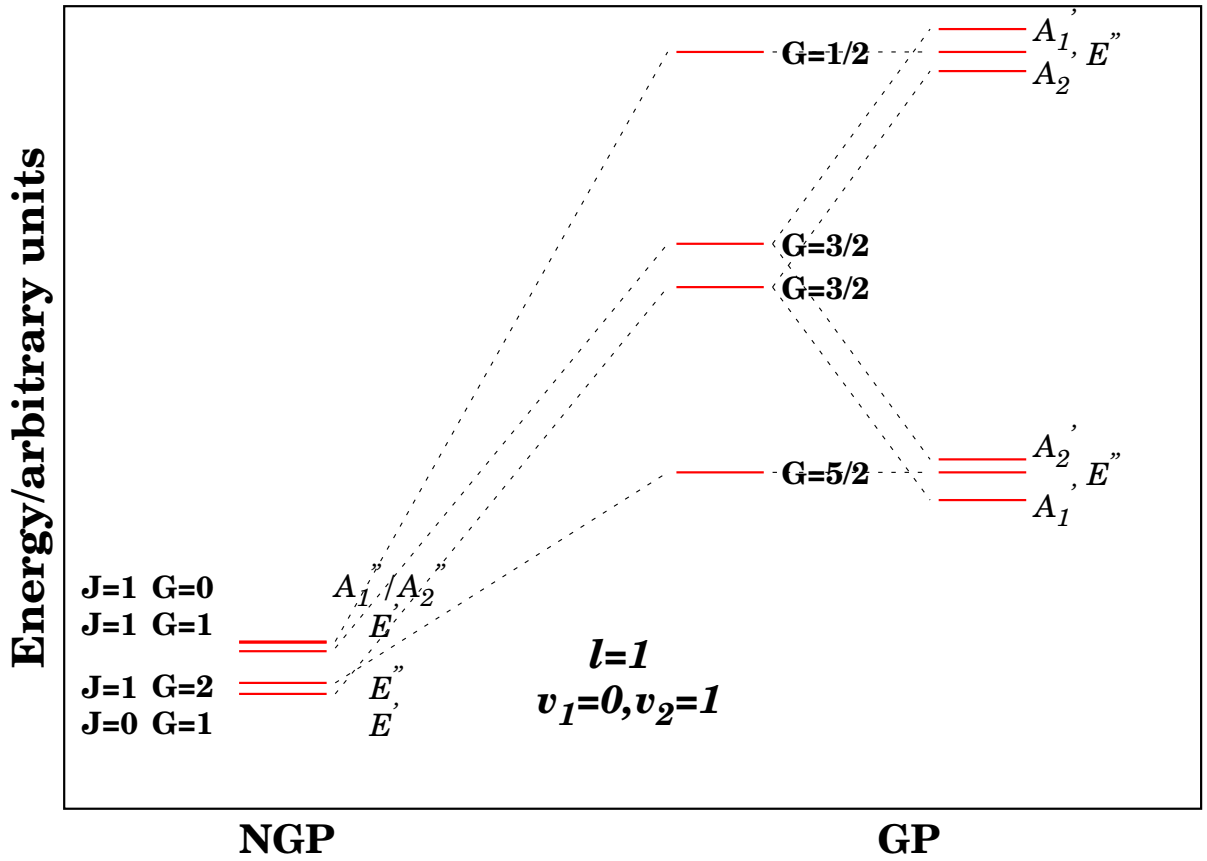


NGP/GP: geometrical phase effect neglected / included; correlation

NGP:	ℓ	$\Gamma(\ell)$	GP:	j	$\Gamma(j)$
	0	A_1'		1/2	E'
	1	E'		3/2	A_1'/A_2'
	2	E'		5/2	E'

Classification of states: a novel quantum number

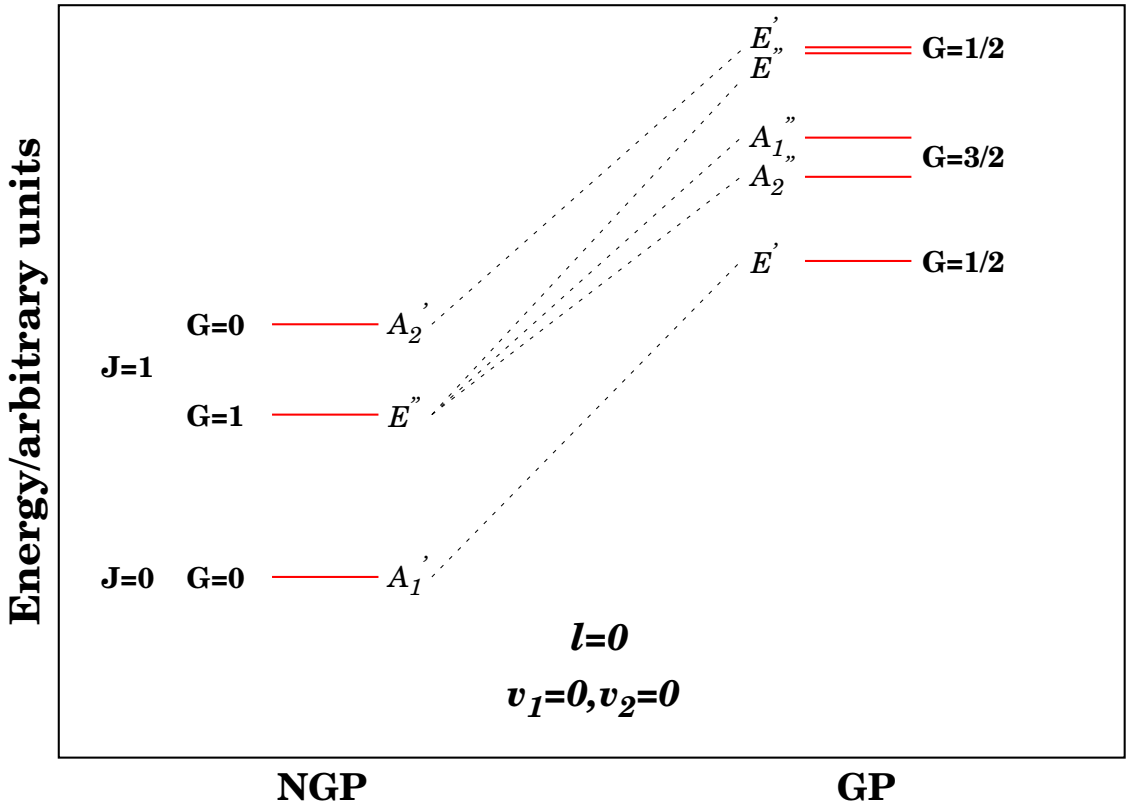
Alijah & Varandas, *Phys. Rev. Lett.* **93**, 243003 (2004)



$$G_{GP} = G_{NGP} + \frac{1}{2}$$

Classification of states: a novel quantum number

Alijah & Varandas, *Phys. Rev. Lett.* **93**, 243003 (2004)



$G_{NGP} = 0 \Leftrightarrow G_{GP} = \frac{1}{2}$; $G_{NGP} = |k| = 1 \Leftrightarrow G_{GP} = G_{NGP} \pm \frac{1}{2} = \frac{3}{2}, \frac{1}{2}$

Rotational structure as a tool for the detection of conical intersections!!

Summary, Acknowledgements & Further Reading

Summary

- H_3^+ is ubiquitous in
  - the atmospheres of hydrogen-rich giant planets
  - interstellar clouds
  - star-forming regions
  - neutron stars?
- Theoretical description
  - difficult due to high accuracy demand
  - requires development of specialized, non-standard methods

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- Dr. Oliver Friedrich (Bielefeld)
- Mihail Cernei (Coimbra)
- Luís Pedro Viegas (Coimbra)

- Fundação para a Ciência e a Tecnologia
- John von Neumann Institut für Computing, Jülich

Further reading

Discussion meetings of the Royal Society London on "Physics, chemistry and astronomy of H_3^+"

- 2000 meeting: *Phil. Trans. R. Soc. A*, **358** 2363-2559 (2000)
- 2006 meeting: *Phil. Trans. R. Soc. A*, **364** 2845-3151 (2006)

The adiabatic approach I

Schrödinger equation:

$$\left[-\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + \sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + V(\mathbf{R},\mathbf{r}) - E_\alpha\right]\Psi_\alpha(\mathbf{R},\mathbf{r}) = 0$$

Adiabatic approach:

$$\Psi_\alpha(\mathbf{R},\mathbf{r}) = \sum_n \Phi_n(\mathbf{R};\mathbf{r})\,\Theta_{n\alpha}(\mathbf{R})$$

Electronic Schrödinger equation:

$$\left[-\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + V(\mathbf{R},\mathbf{r}) - \epsilon_n(\mathbf{R})\right]\Phi_n(\mathbf{R},\mathbf{r}) = 0$$

Nuclear Schrödinger equation:

$$\sum_n \left\{\left[-\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + \epsilon_n(\mathbf{R}) - E_\alpha\right]\delta_{n'n} + C_{n'n}(\mathbf{R}) + D_{n'n}(\mathbf{R})\right\}\Theta_{n\alpha}(\mathbf{R}) = 0$$

The adiabatic approach II

Nuclear Schrödinger equation:

$$\sum_n \left\{ \left[-\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + \epsilon_n(\mathbf{R}) - E_\alpha \right] \delta_{n'n} + C_{n'n}(\mathbf{R}) + D_{n'n}(\mathbf{R}) \right\} \Theta_{n\alpha}(\mathbf{R}) = 0$$

$$C_{n'n}(\mathbf{R}) = -\sum_I \frac{\hbar^2}{2M_I} \left\langle \phi_{n'}(\mathbf{R};\mathbf{r}) | \nabla_I^2 \phi_n(\mathbf{R};\mathbf{r}) \right\rangle_{\mathbf{r}}$$

$$D_{n'n}(\mathbf{R}) = -\sum_I \frac{\hbar^2}{2M_I} \left\langle \phi_{n'}(\mathbf{R};\mathbf{r}) | \nabla_I \phi_n(\mathbf{R};\mathbf{r}) \right\rangle_{\mathbf{r}} \nabla_I$$

For a single surface:

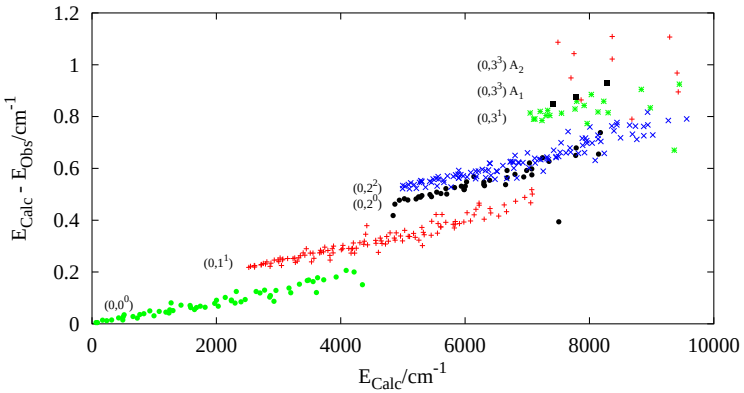
$$\left[-\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + \epsilon_n(\mathbf{R}) + C_{nn}(\mathbf{R}) - E_\alpha \right] \Theta_{n\alpha}(\mathbf{R}) = 0$$

- Diagonal correction $C_{nn}(\mathbf{R})$ very important
- Can the effect of $C_{n'n}$ & $D_{n'n}$ be simulated by a constant empirical mass?

Simulation of non-adiabatic effects: H_3^+

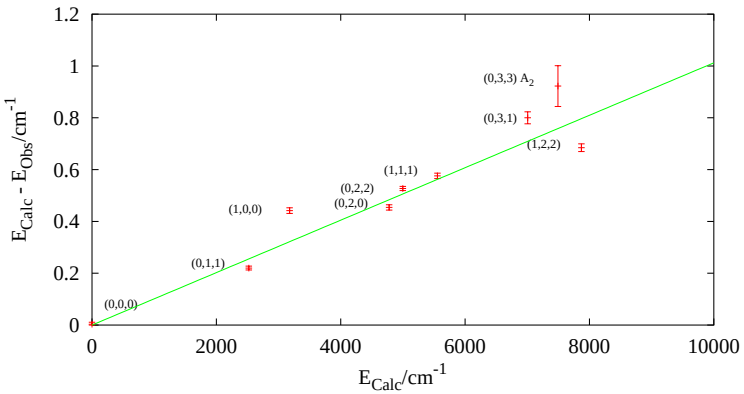
Schiffels, Alijah & Hinze, *Molec. Phys.* **101**, 175 (2003), *ibid.* **101**, 189 (2003)

- Determination of parameters



$$\begin{aligned} \Delta E &= E_{calc} - E_{obs} \\ &= a_0 + a_1\, J(J+1) + a_2\, G^2 \\ E^{(1)}_{corr} &= E_{calc} - a_0 - a_1\, J(J+1) - a_2\, G^2 \end{aligned}$$

- Extrapolation



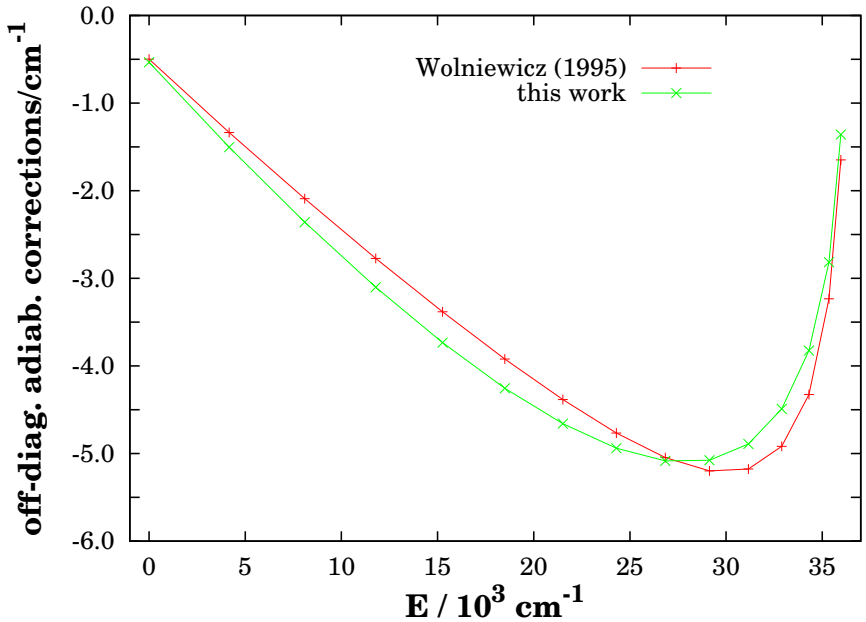
$$\begin{aligned} a_0 &= b_1\, E^0_{calc} \\ E^{(2)}_{corr} &= E_{calc} - b_1 E^0_{calc} \\ &\quad -\bar{a}_1\, J(J+1) - \bar{a}_2\, G^2 \\ E^{(4)}_{corr} &= E_{calc} - b_1 E_{calc} \end{aligned}$$

Non-adiabatic corrections: H_2

Alijah & Hinze, *Phil. Trans. R. Soc. A*, **364**, 2877 (2006)

$$\Delta E = c \frac{n\, m_e}{M_N} \left\langle \frac{dV_J(R)}{dR} (R - R_e) \right\rangle$$

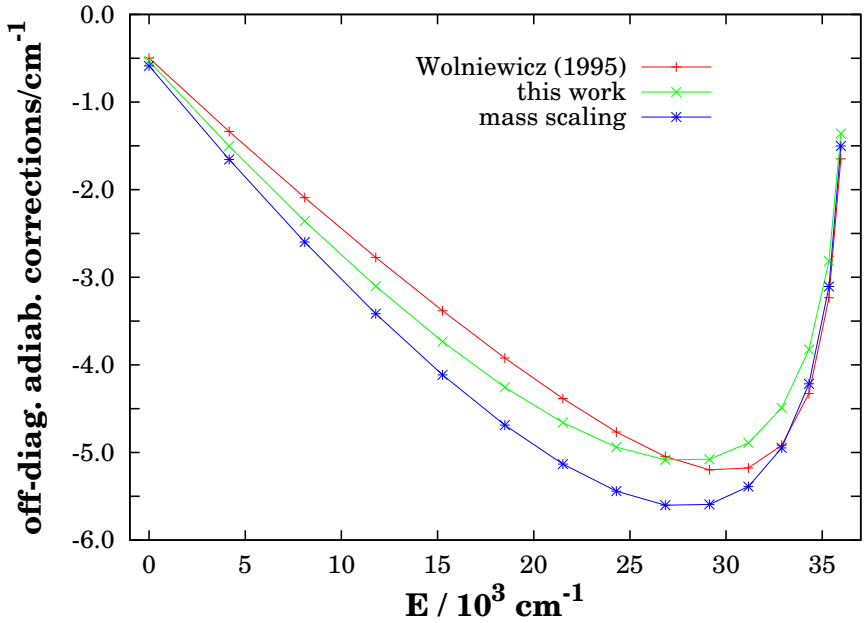
$c = 0.11$, a universal parameter



At high energies $\Delta E \approx 0$ because $\lim_{R \to \infty} dV/dR = 0$

Non-adiabatic corrections: H_2

A. Alijah, work in progress

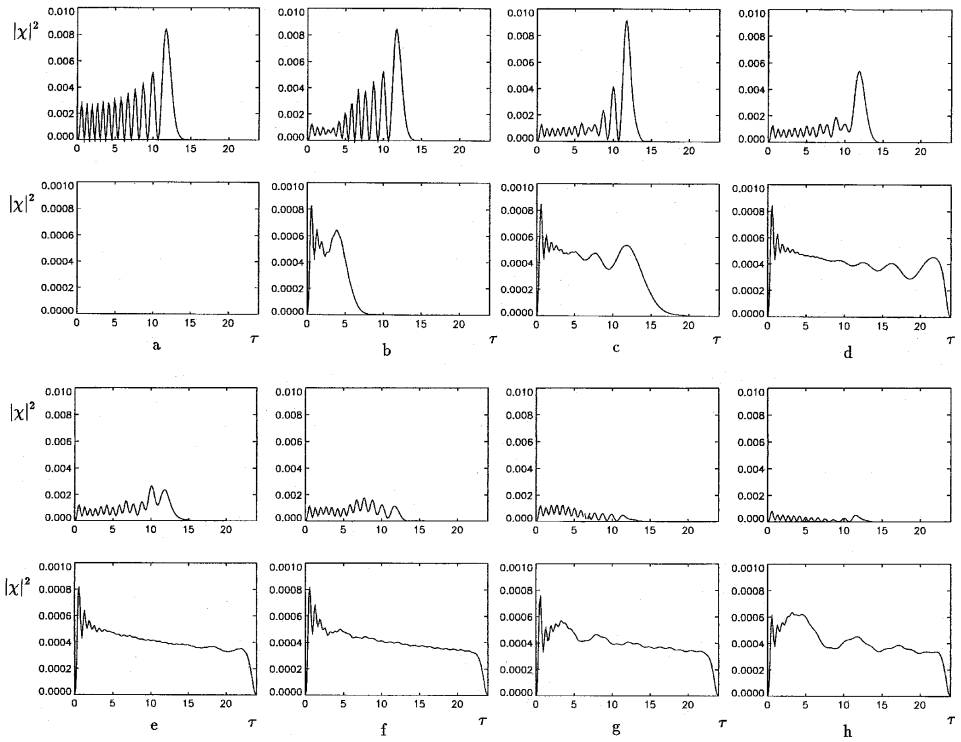


Comparison of two approaches:

- present approach: $\chi^2 = 0.30\,\mathrm{cm}^{-1}$
- atomic masses approach: $\chi^2 = 0.49\,\mathrm{cm}^{-1}$

Decay of Słonczewski resonances

Alijah & Nikitin *Molec. Phys.* **96**, 1399 (1999)
Model study



Time evolution of a wave packet on two surfaces

$\longrightarrow$ Wave packet maintains its form during decay

Classification of states: a novel quantum number

Alijah & Varandas, *Phys. Rev. Lett.* **93**, 243003 (2004)

$$
\begin{aligned}
|v_1 v_2 GN\rangle_{\pm} &= \frac{1}{\sqrt{2}}\left(|v_1 v_2, \ell+\alpha\rangle\,|Nk\rangle \pm (-1)^N |v_1 v_2, -\ell-\alpha\rangle\,|N,-k\rangle\right) \\
&= \frac{1}{\sqrt{2}}\left(|v_1 v_2 \ell\rangle\,|Nk\rangle \pm (-1)^N |v_1 v_2, -\ell-2\alpha\rangle\,|N,-k\rangle\right) e^{i\alpha\phi}
\end{aligned}
$$

generalized G quantum number:

$$
G = |k-\ell-\alpha| = |k-j| \quad ; \quad |j| = |\ell| + \alpha \quad ; \quad \alpha = 0, 1/2
$$

NGP/GP correlation:

- for $\ell = 0$ (special case)

$$
G_{NGP} = 0 \quad \Leftrightarrow \quad G_{GP} = \frac{1}{2}
$$

$$
G_{NGP} = |k| \neq 0 \quad \Leftrightarrow \quad G_{GP} = G_{NGP} \pm \frac{1}{2}
$$

- for $\ell \neq 0$

$$
G_{GP} = G_{NGP} + \frac{1}{2}
$$