H_3^+ in the electronic triplet state

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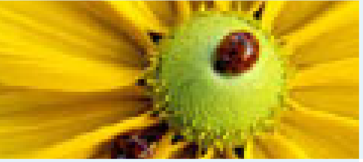
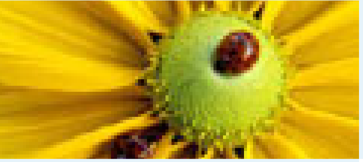
Introduction



The $1^3E'$ state

- Hirschfelder
  J. Chem. Phys. **6**, 795 (1938)
- Pfeiffer, Huff, Greenawalt & Ellison
  J. Chem. Phys. **46**, 821 (1967)
- Kawaoka & Borkman
  J. Chem. Phys. **54**, 4234 (1971)
- Schaad & Hicks
  J. Chem. Phys. **61**, 1934 (1974)
  stable electronic state: $a\,^3\Sigma_u^+$
- Ahlrichs, Votava & Zirc
  J. Chem. Phys. **66**, 2771 (1977)
- Wormer & de Groot
  J. Chem. Phys. **90**, 2344 (1989)
- Preiskorn, Frye & Clementi
  J. Chem. Phys. **94**, 7204 (1991)



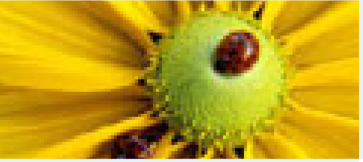
Comments

- "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."
  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."
  Tennyson, *Rep. Prog. Phys.* **57**, 421 (1995)

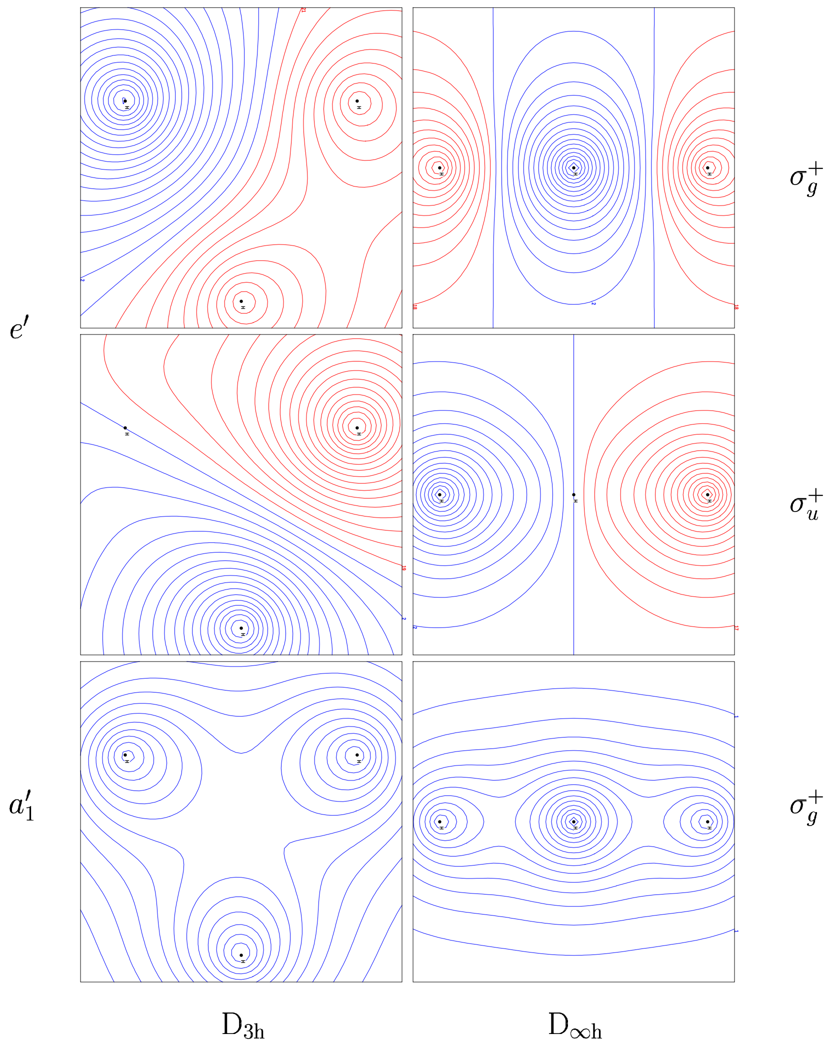
First ro-vibrational calculations

- Friedrich, Alijah, Xu & Varandas,
  Phys. Rev. Lett. **86**, 1183 (2001)
- Sanz, Roncero, Tablero, Aguado & Paniagua,
  J. Chem. Phys. **114**, 2182 (2001)

Potential energy surfaces

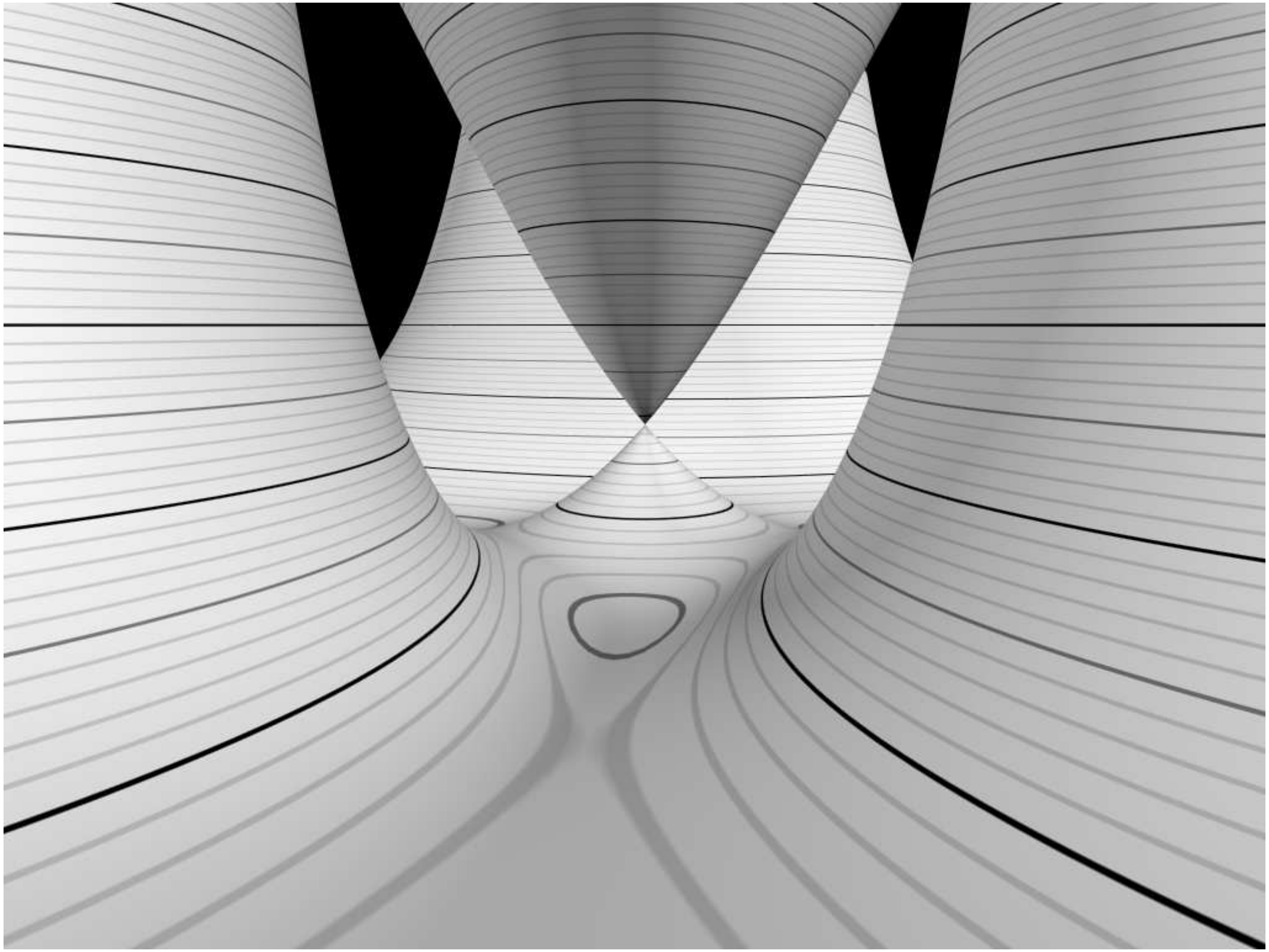


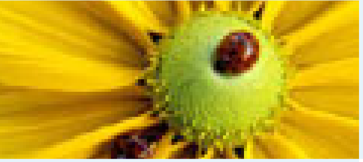
Molecular orbitals



config.	states	
	D_{3h}	$D_{\infty h}$
$a_1'^{\,2}$	$X\,^1A_1'$	
$a_1'e'$	$a\,^3E'$	$\rightarrow (^3\Sigma_u^+,\ ^3\Sigma_g^+)$
	$A\,^1E'$	

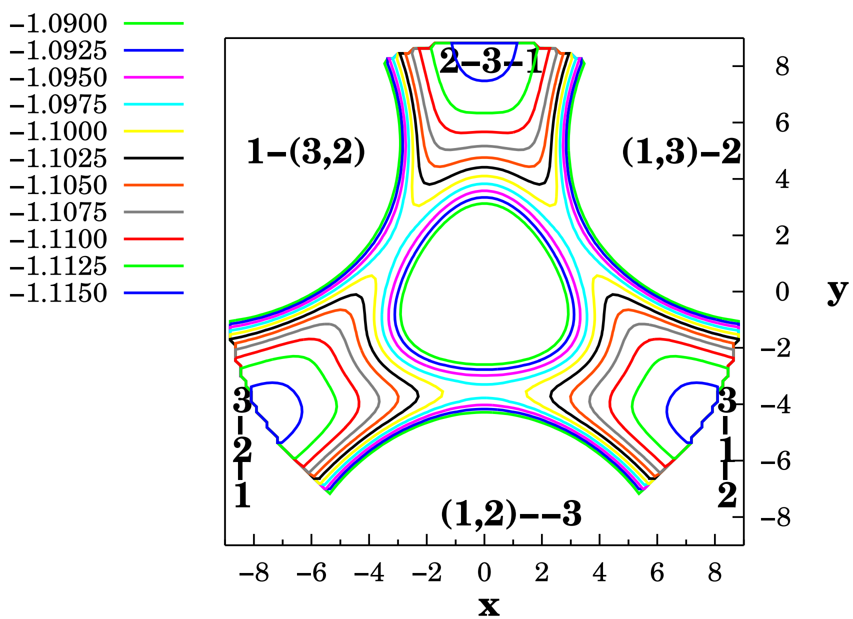
View of the surfaces





Characteristics of the surfaces

- upper branch:
  dissociation: $2\mathrm{H}\,(^2\mathrm{S}) \;+\; \mathrm{H}^+$, $-1.0000\,\mathrm{E_h}$
  energy minimum (D_{3h}): $-1.034590\mathrm{E_h}$ at $3.610\,\mathrm{a_0}$
- lower branch:
  dissociation: $\mathrm{H}_2^+\,(^2\Sigma_g^+) \;+\; \mathrm{H}\,(^2\mathrm{S})$, $-1.1026\,\mathrm{E_h}$
  energy minimum ($D_{\infty h}$): $-1.11610627\mathrm{E_h}$ at $2.454\,\mathrm{a_0}$



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

Van der Waals complex

```
            H
H · · · · · |⊕
            H
```

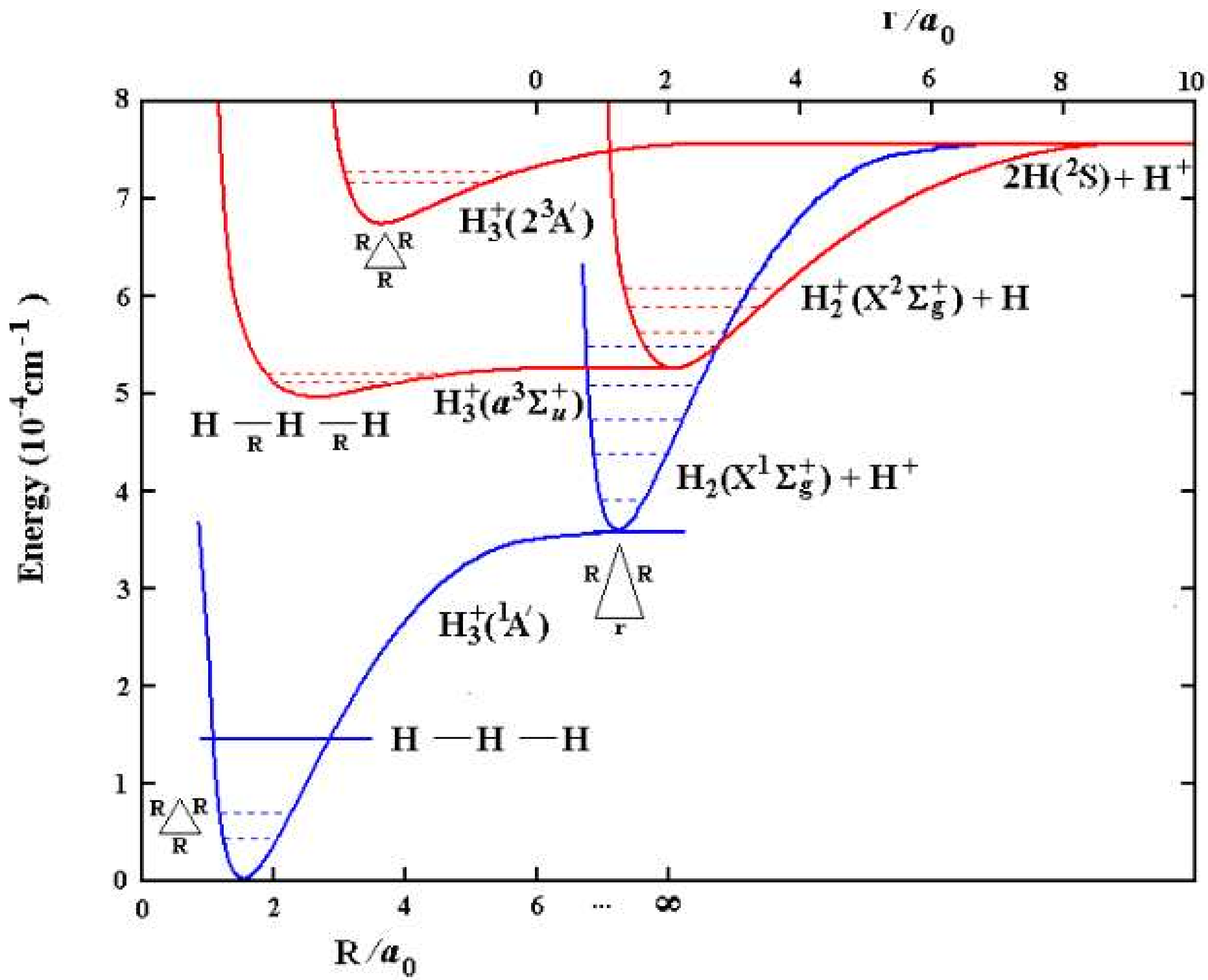
Comparison of ab initio calculations

group	r/a_0	E_{min}/E_h	basis
Schaad & Hicks	2.457	-1.114 22	21
Wormer & de Groot	2.45	-1.114 66	60[a)]
Ahlrichs, Votava & Zirc	2.4568	-1.115 678 7	45
Preiskorn, Frye & Clementi	2.454	-1.116 102 7	102[b)]
Friedrich, Alijah, Xu & Varandas	2.4537	-1.116 061	165
Sanz, Roncero, Tablero, Aguado & Paniagua	2.454	-1.116 106 27	489[c)]

[a)] only 42 functions used for PES
[b)] Hylleraas-CI
[c)] only 108 functions used for PES

Tunneling Barrier:
11.78 $mE_h = 2585\ cm^{-1}$ (Wormer & de Groot)
11.84 $mE_h = 2598\ cm^{-1}$ (Friedrich *et al.*)
12.03 $mE_h = 2640\ cm^{-1}$ (Sanz *et al.*)

Electronic states



Energy minimum paths

Representations of potential energy surfaces

Friedrich, Alijah, Xu & Varandas, *Phys. Rev. Lett.* **86**, 1183 (2001)

$$V(\rho,\theta,\phi) = V_{Coulomb} + V_{D_{3h}}(\rho) + \frac{\sum_{ij} a_{ij}(\rho)\sin^i\theta\sin^j 3\phi}{1+\left[\sum_{ij} b_{ij}(\rho)\sin^i\theta\sin^j 3\phi\right]^2}$$

Sanz, Roncero, Tablero, Aguado & Paniagua, *J. Chem. Phys.* **114**, 2182 (2001)

$$V(\mathbf{R}) = V_{DIM}(\mathbf{R}) + V^{(3)}(\mathbf{R})$$

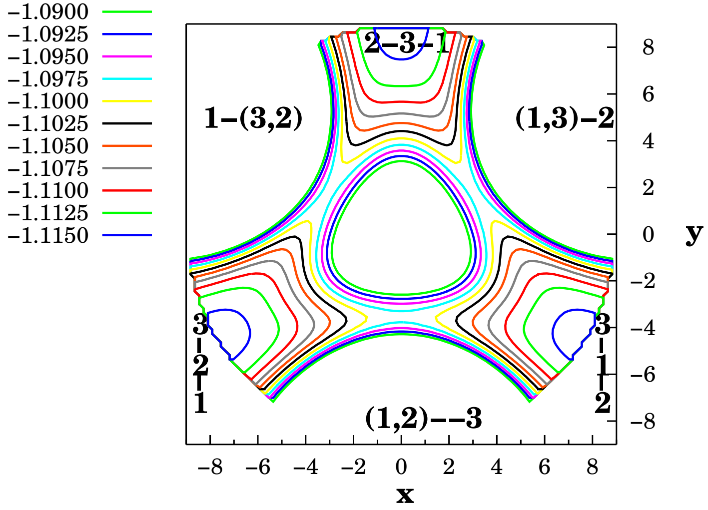
Cernei, Viegas, Alijah & Varandas
J. Chem. Phys. **118**, 2637 (2003)
J. Chem. Phys. **120**, 2053 (2004)
Chem. Phys. **308**, 2085 (2005)

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

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

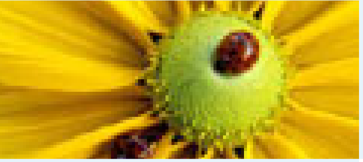
Ro-vibrational states on the lower sheet

Localised vs. non-localised states



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

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



Method of hyperspherical harmonics

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

Schrödinger equation:

$$\left\{ T(\rho) + \frac{\Lambda^2(\Omega)}{2\mu\rho^2} + V(\rho,\theta,\phi) - E_k \right\} \Phi_k(\rho,\Omega) = 0$$

Hyperspherical harmonics:

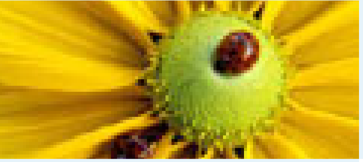
$$\Lambda^2\Psi = K(K+4)\Psi \quad ; \qquad -i\frac{\partial}{\partial\phi}\Psi = \frac{\nu}{2}\Psi$$

Expansion:

$$\Phi_k(\rho,\Omega) = \sum_j \Psi_j(\Omega) R_{jk}(\rho)$$

Coupled radial equations:

$$\left[\sum_j \left(T(\rho) + \frac{K(K+4)}{2\mu\rho^2} \right) \delta_{jk} + \langle \Psi_j | V | \Psi_k \rangle - E_k \delta_{jk} \right] R_{jk}(\rho) = 0$$



Spectroscopic assignment of hyperspherical states

Alijah, Wolniewicz & Hinze, *Molec. Phys.* **85**, 1125 (1995)

Features: wavefunctions not needed, Dunham fits not needed

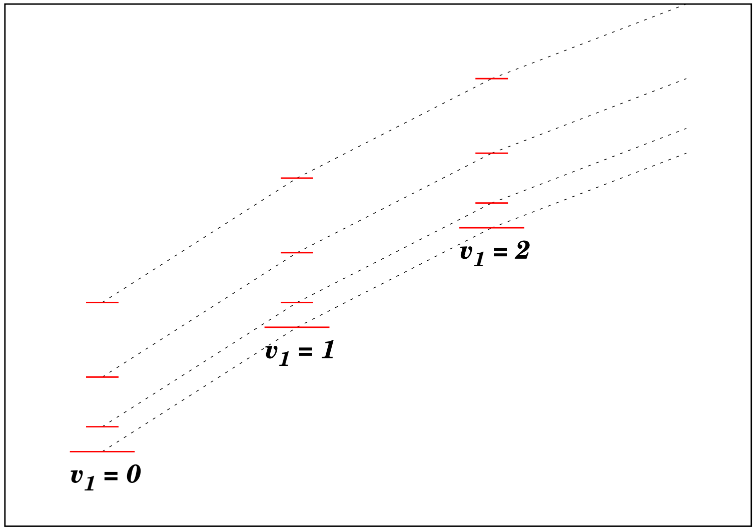
$$\textit{hyperspherical states} \Longrightarrow S_N \times I \Longleftarrow \textit{spectroscopic states}$$

Algorithm:

- Given a set of hyperspherical states $|\Gamma, J, n\rangle$, where Γ denotes permutation-inversion symmetry in $S_N \times I$
- Given the symmetry properties, Γ, of spectroscopic states $|v_1, v_2, \ldots, J\rangle$
- loop over vibrational quantum numbers v_i
    - determine band origin, $|v_1, v_2, \ldots, J = 0\rangle$, choosing a hyperspherical state with appropriate Γ

Algorithm: continuation

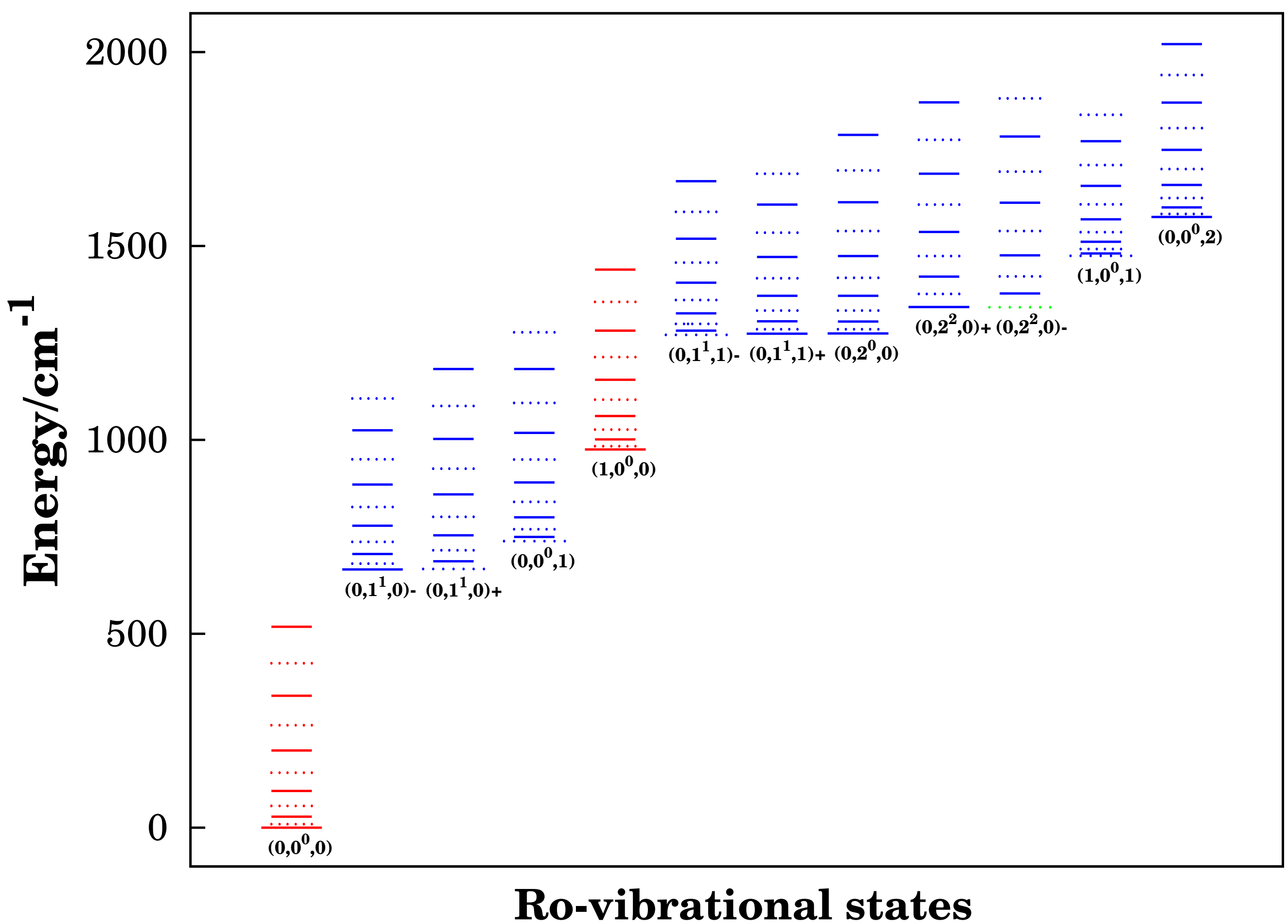
- loop over J
  - find $|\Gamma, J, n\rangle$ that represents $|v_1, v_2, \dots, J\rangle$ subject to
    - correct Γ
    - $E(J+1) > E(J)$
    - observation of trends within families of states: $|v_1, v_2, \dots, J\rangle$, $|v_1+1, v_2, \dots, J\rangle$, $|v_1+2, v_2, \dots, J\rangle$, ... where ν_1 denotes the totally symmetric vibration



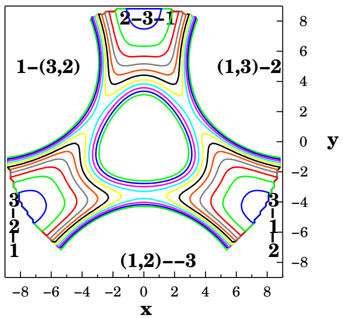
Results for H_3^+: I

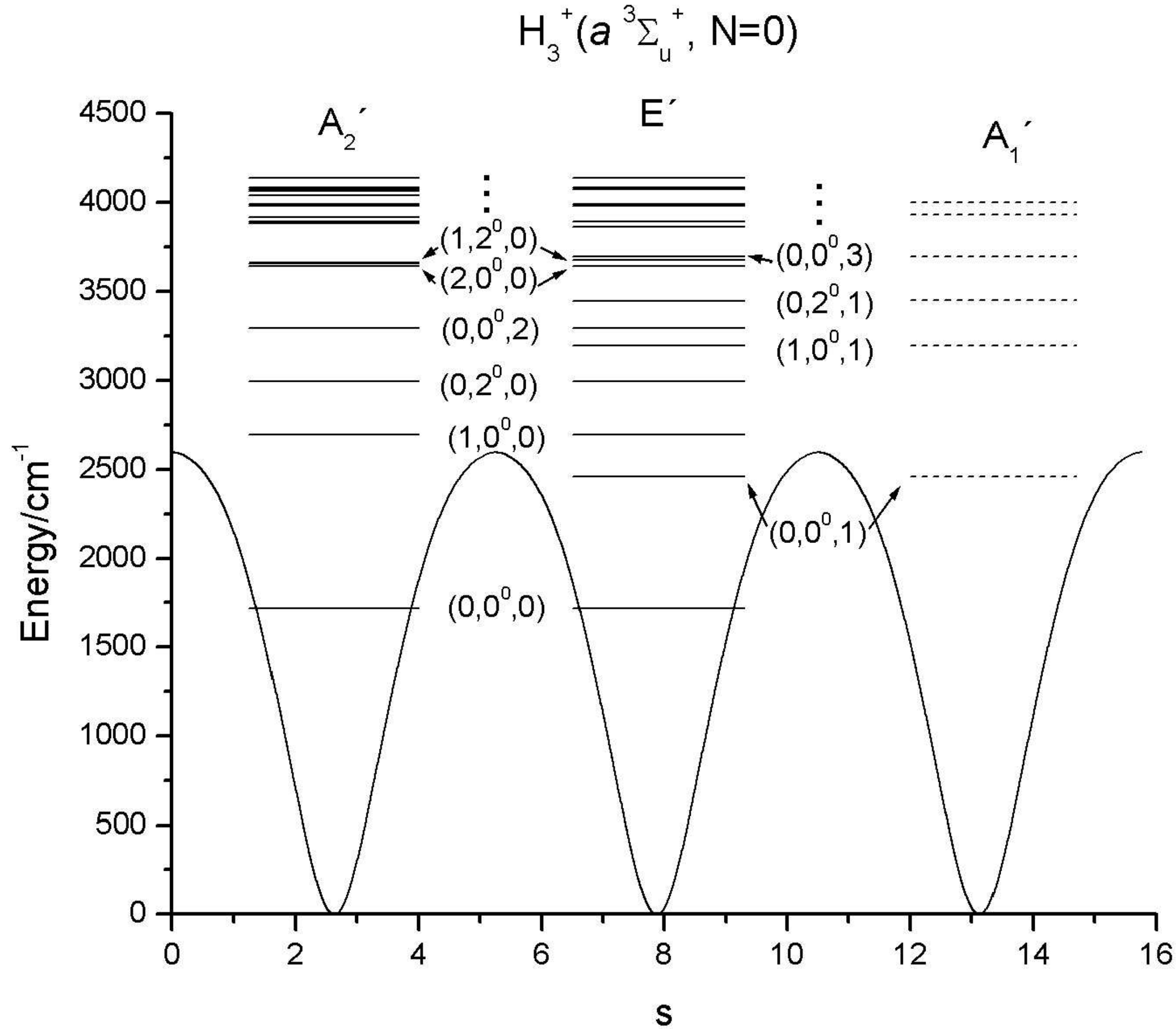
Alijah, Viegas, Cernei & Varandas, *J. Mol. Spectrosc.* **221**, 163 (2003)

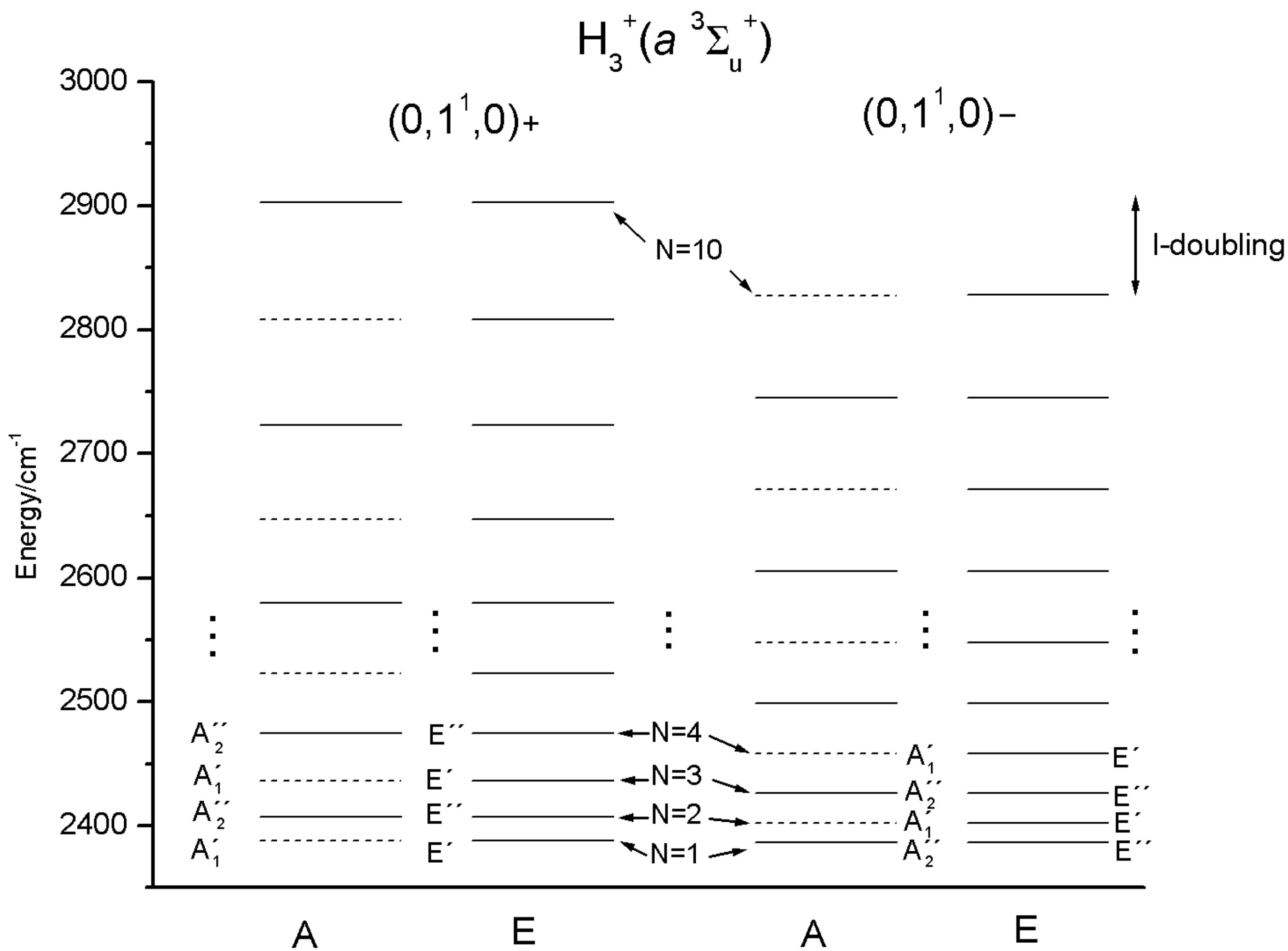
560 ro-vibrational states identified ($J \leq 10$)



Results for H_3^+: II

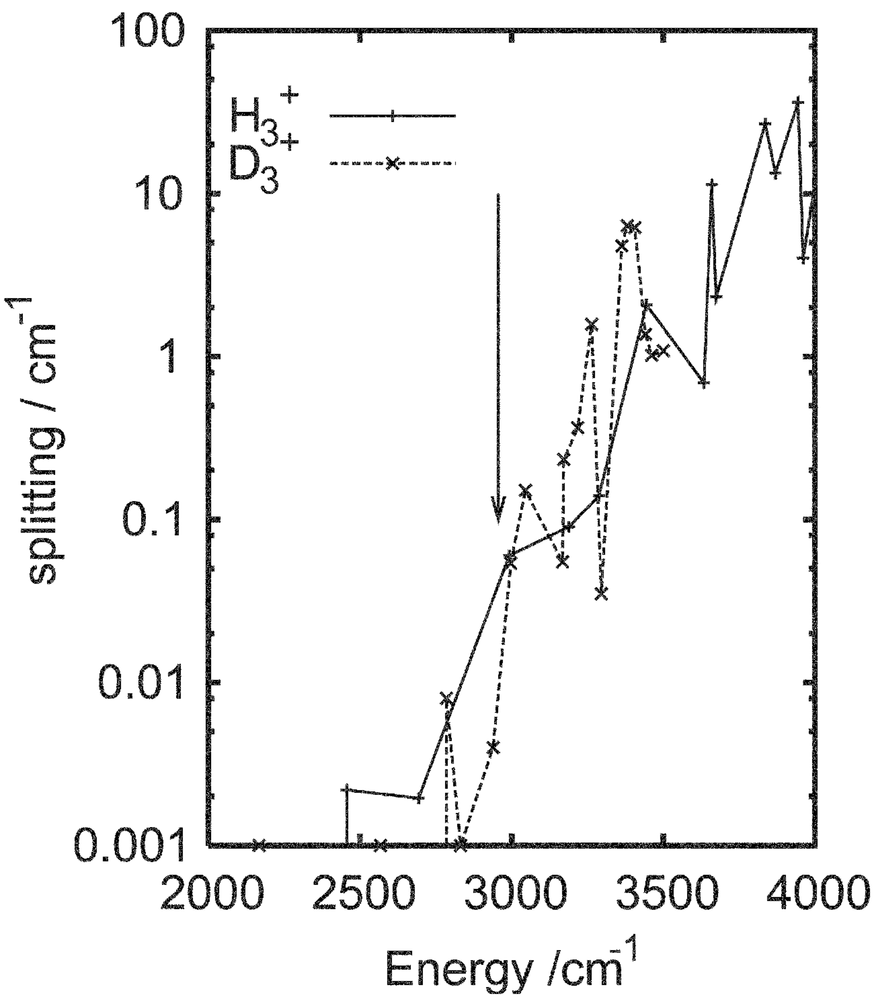





$H_3^+(a\ ^3\Sigma_u^+)$
$(0,1^1,0)+$
$(0,1^1,0)-$
Energy/cm^{-1}
3000
2900
2800
2700
2600
2500
2400
N=10
l-doubling
N=4
N=3
N=2
N=1
A_2''
A_1'
A_2''
A_1'
E''
E'
E''
E'
A_1'
A_2''
A_1'
A_2''
E'
E''
E'
E''
A
E
A
E

Results for D_3^+: vibrational states

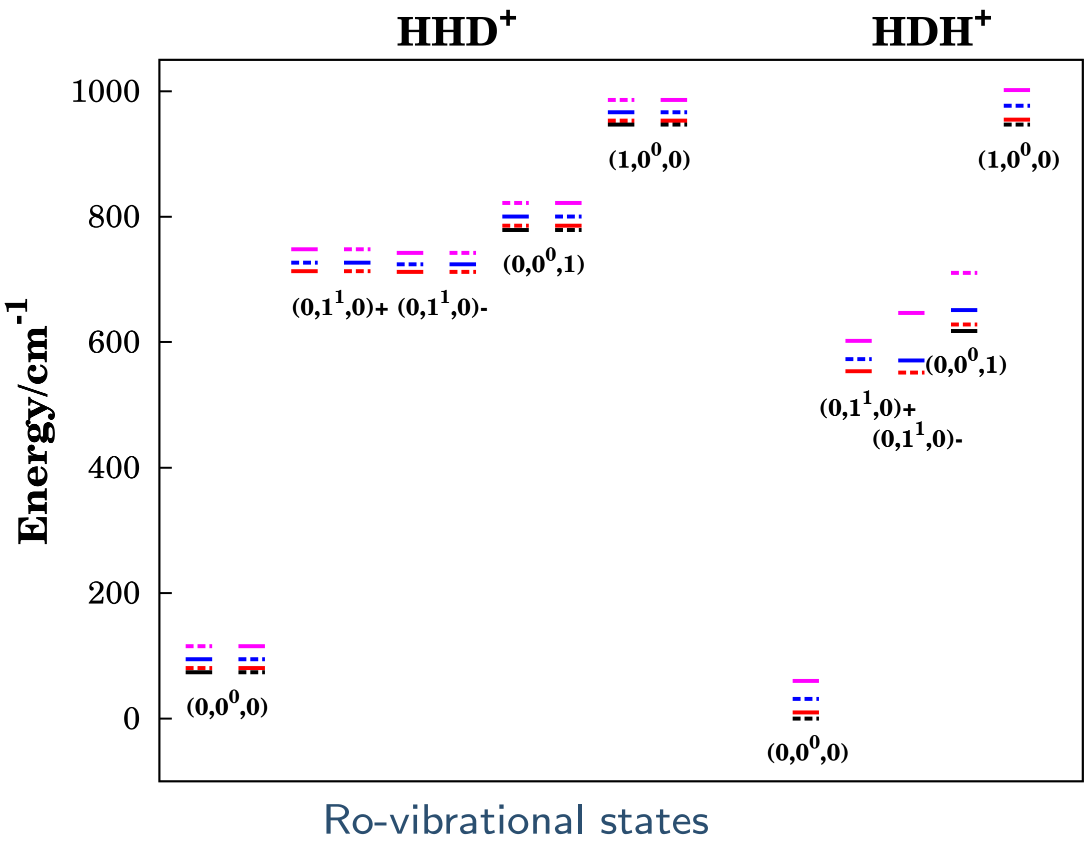
Cuervo-Reyes, Rubayo-Soneira, Aguado, Paniagua, Tablero, Sanz & Roncero, *Phys. Chem. Chem. Phys.* **4**, 6012 (2002)

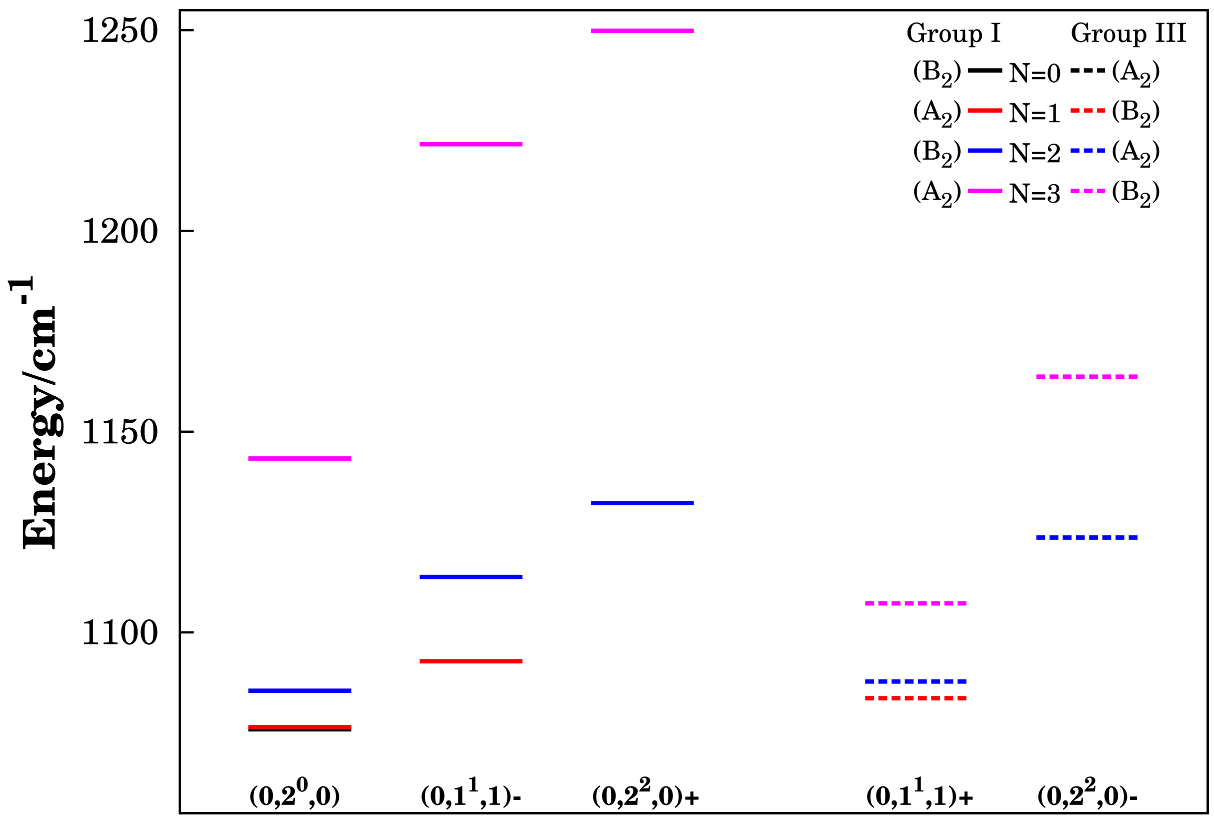


Results for H_2D^+: ro-vibrational states

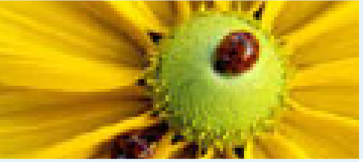
Alijah & Varandas, *J. Phys. Chem. A* (2006)

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





Ro-vibrational states of HDH$^+$



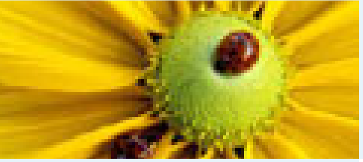
Transition frequencies

molecule	initial state	$\Gamma_{rve}(w)$	final state	$\Gamma_{rve}(w)$	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:

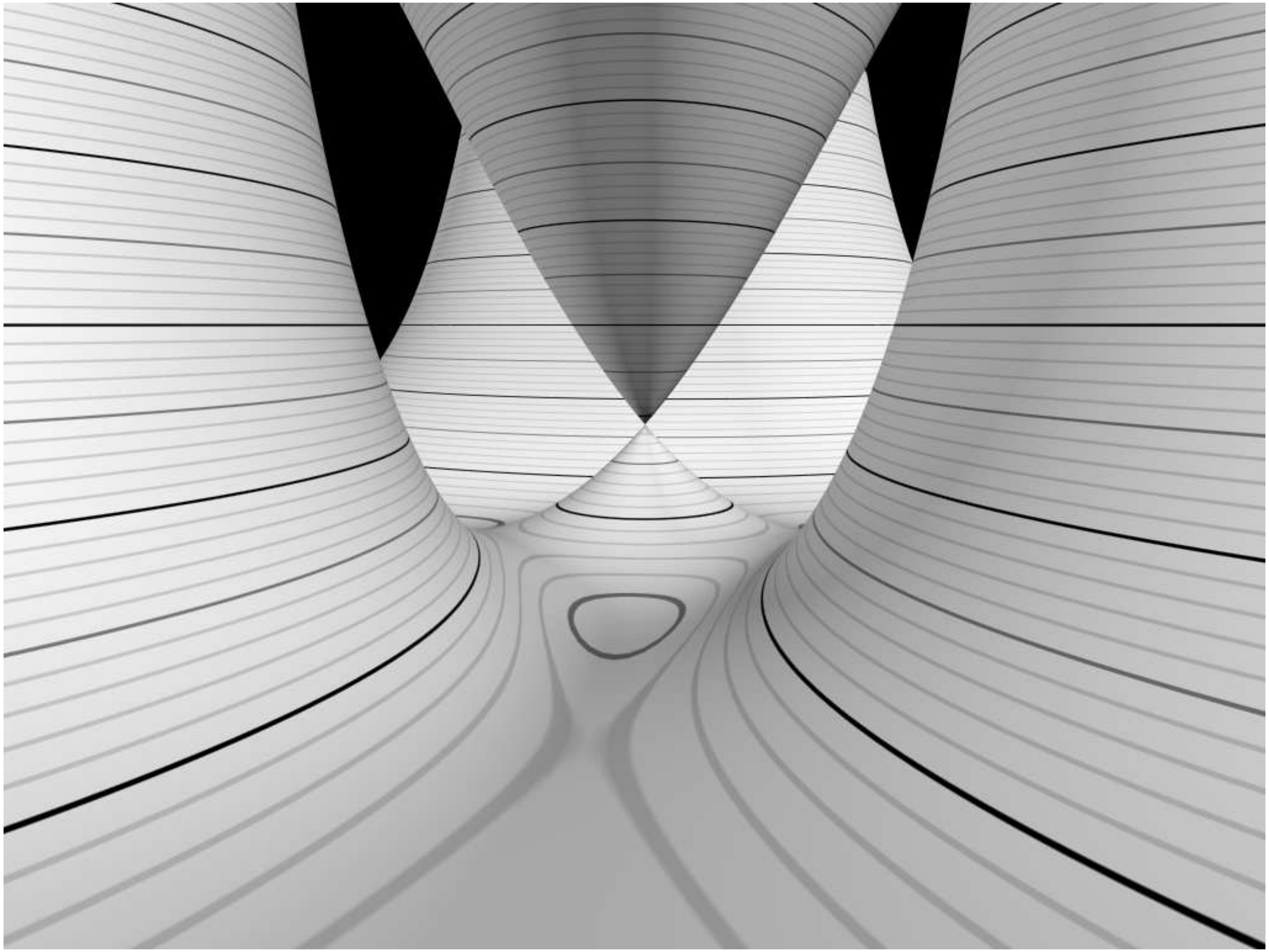
H_3^+, D_3^+ $\Delta J = 0, \pm 1$ $A_1' \leftrightarrow A_1''$, $A_2' \leftrightarrow A_2''$, $E' \leftrightarrow E''$

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



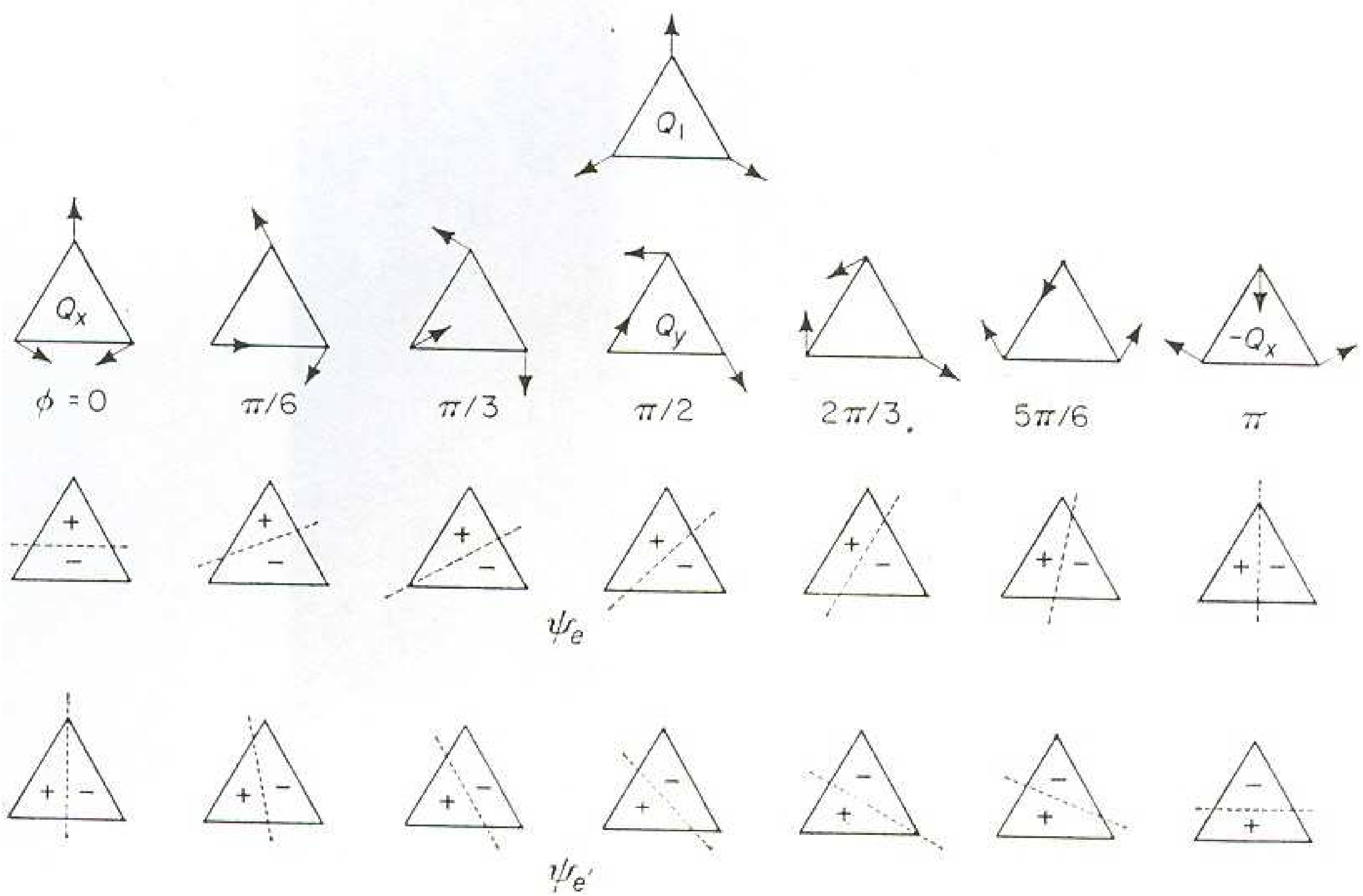
Ro-vibrational states on the upper sheet

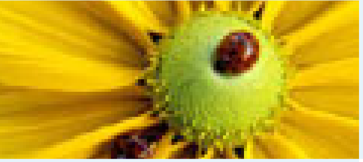
View of the surfaces



The geometrical phase

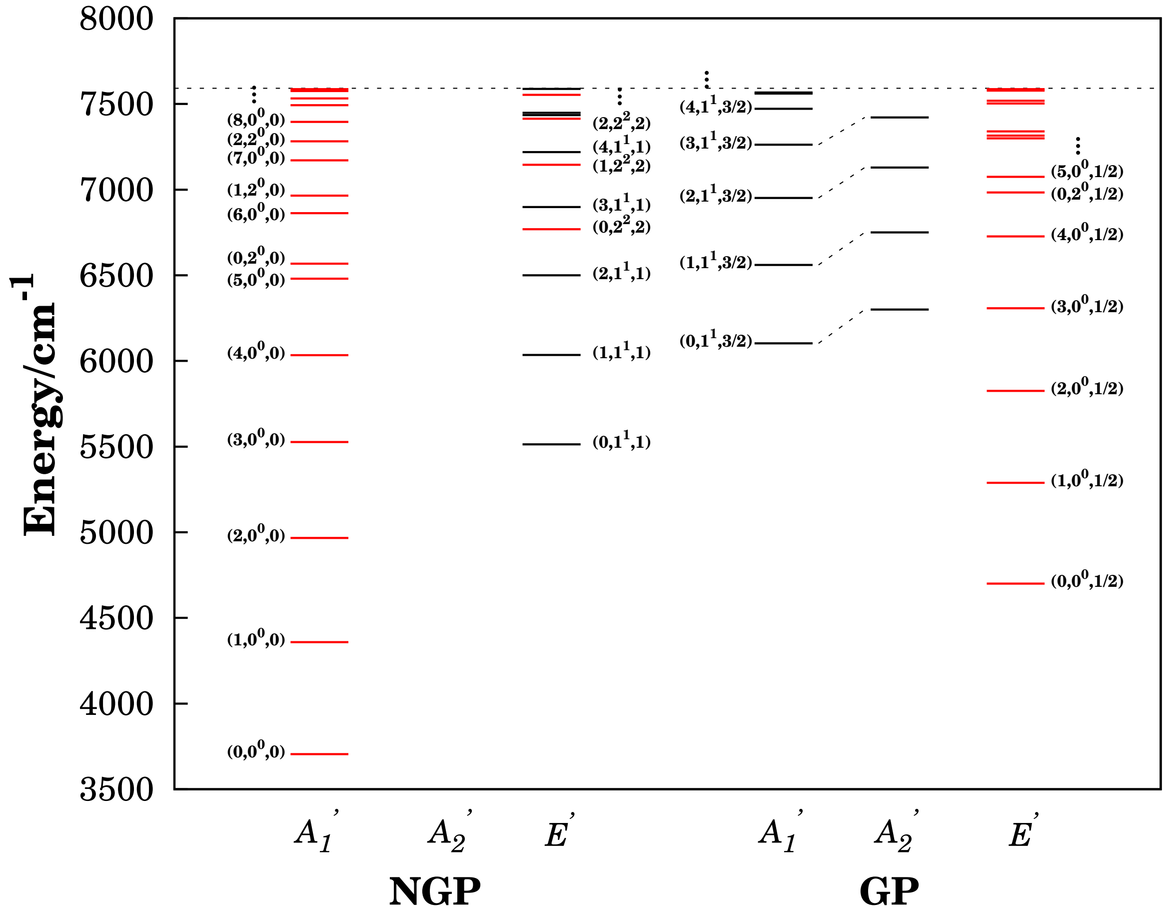
Longuet-Higgins, *Adv. Spectrosc.* **2**, 429 (1961)



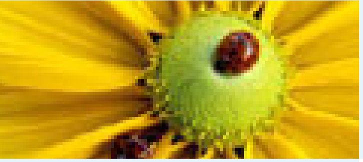


Vibronic Slonczewski resonance states

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



Semiclassical lifetimes: Nikitin, *J. Chem. Phys.* **107**, 6748 (1997)



Classification of ro-vibronic cone states

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

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

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)

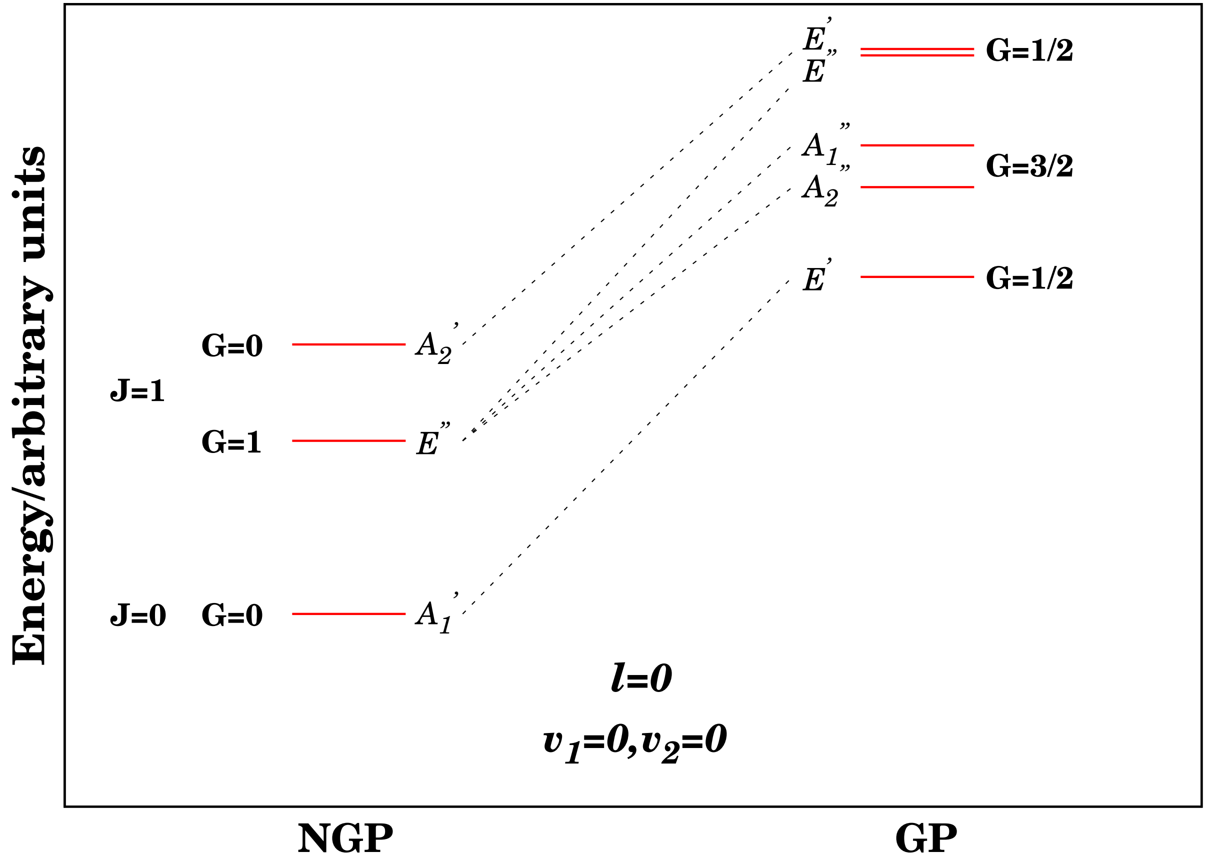
$$G_{NGP} = 0 \quad \Leftrightarrow \quad G_{GP} = \frac{1}{2}$$

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

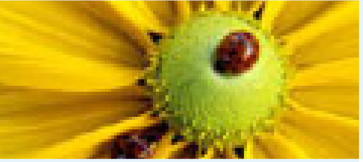
- for $\ell \neq 0$

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

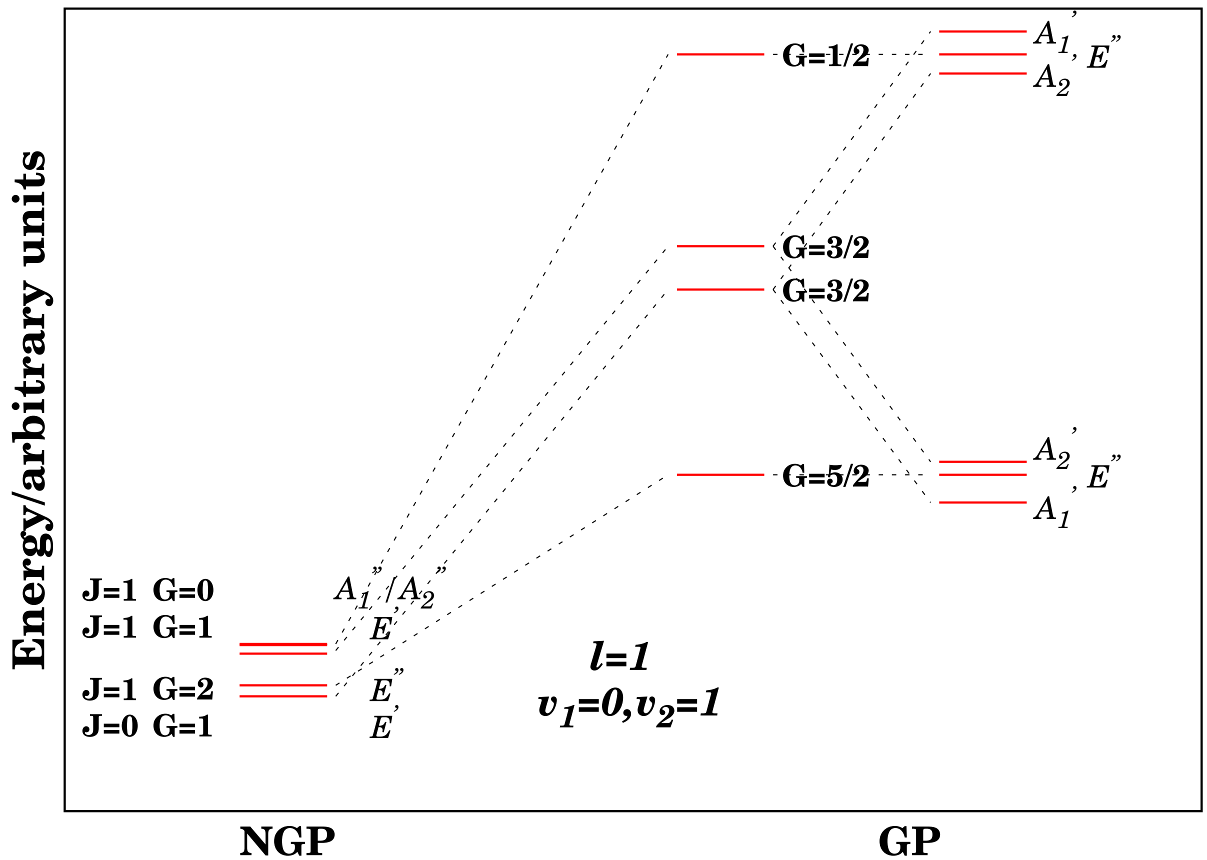
Ro-vibronic cone states I



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



Ro-vibronic cone states II

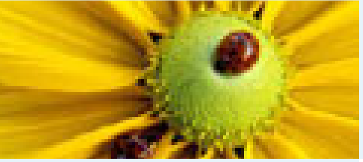


$$G_{GP} = G_{NGP} + \frac{1}{2}$$

Conclusions

Experiments?

- Theoretical data available
- Experimental data?
  - Excitation from the ground state $(X\,^1A_1')$
  - $\mathrm{H_2^+}(\mathrm{X}\,^2\Sigma_g^+) + \mathrm{H}$, aligned in an external field
  - $\mathrm{H_2}(\mathrm{b}\,^3\Sigma_u^+) + \mathrm{H^+}$
  - $\ldots$



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