

#### And now for something completely different...



Local modes in vibrational (and rotational) spectroscopy

#### (Picture courtesy of Python M)







### The Wuppertal monorail





#### Vibrational energies of small molecules



The lowest vibrational energies for several simple molecules.







### H-X stretching vibrations modelled by Morse oscillators:

Hamiltonian:  $\widehat{H}_{Morse}^{(j)} = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r_i^2} + V_{Morse}(r_j).$  $\mu = \frac{m_{\rm H} m_{\rm X}}{m_{\rm H} + m_{\rm X}}$ 6.0 5.0 4.0 energy (eV) 3.0 Do  $V_{\text{Morse}}(r_j) = D_e y_j^2$ D۵ 2.0 1.0  $y_i = 1 - \exp(-a[r_i - r_e]).$ 0.0 0.0 1.0 2.0 3.0 4.0 5.0 R (Å) Copyright 2000 B.M. Tissue 

EIGENVAIUES:  

$$\omega_{\rm M} = \frac{a}{2 \pi c} \sqrt{\frac{2 D_{\rm e}}{\mu}} \quad x_{\rm M} = -\frac{a^2 \hbar}{4 \pi \mu c} < 0.$$

$$E_{n_j}/bc = \omega_{\rm M} \left[ n_j + \frac{1}{2} \right] + x_{\rm M} \left( n_j + \frac{1}{2} \right)^2,$$
  
$$n_j = 0, 1, 2, 3, \dots$$



#### HCAO model for H<sub>2</sub>X molecule stretch (Harmonically Coupled Anharmonic Oscillators)

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## Diagonalized in basis set of products of Morse-oscillator eigenfunctions

[1] Child MS, Lawton RT. *Faraday Discuss Chem Soc* 1981, 71:273–285.
[2] Mortensen OS, Henry BR, Mohammadi MA. *J Chem Phys* 1981, 75:4800–4808
[3] Child MS, Halonen L. *Adv Chem Phys* 1984, 57:1–58



#### **HCAO** matrices



**FIGURE 2** Schematic representation of the HCAO energy matrix for N = 4. The horizontal lines represent the diagonal matrix elements and the off-diagonal elements are indicated. Note that, by definition, the parameter  $x_{\rm M} < 0$ .

$$\lambda = \frac{\omega_{\rm M}}{2} \left( \frac{C_{rr'}}{2 D_{\rm e}} - \frac{m_{\rm H}}{m_{\rm H} + m_{\rm X}} \cos \rho_{\rm e} \right).$$



**FIGURE 3** | Schematic representation of the HCAO energy matrix for N = 5. The horizontal lines represent the diagonal matrix elements and the off-diagonal elements are indicated. Note that by definition, the parameter  $x_{\rm M} < 0$ .

#### Vibrational energies patterns: Normal mode, Local mode...





**Vibrational intensities** 

Empirical fact: Stretching part of

dipole moment function modelled

well by "Molecular Bond" function





## Favours vibrational transitions to states with all *N* excitation quanta localized in one bond.

[1] HALONEN, L., 1998, Adv. chem. Phys., **104**.





#### **Summary:**

Excited stretching states form "polyads" with the structure predicted by HCAO



Observed transitions from the vibrational ground state end in lowest levels of polyad.

Results transferable to molecules with n > 2 equivalent H-X stretching vibrations.



## Example experiment: ICLAS

(Intracavity Laser Absorption Spectroscopy)



- Extremely sensitive
- Absoption path lengths of order-of-magnitude 100 km

Campargue A: <u>http://www.chem.uni-wuppertal.de/sphers/han-sur-lesse/campargue/camparguenew.html</u>
 Bertseva E, Kachanov AA, Campargue A. *Chem Phys Lett* 2002, 351:18–26.



## **Example experiment: ICLAS for H<sub>2</sub>S**

(Intracavity Laser Absorption Spectroscopy)



[1] Ding Y, Naumenko O, Hu S-M, Bertseva E, Campargue A. J Mol Spectrosc 2003, 217:222–238.



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### **Rotational Energy Level Clusters**

- 1972 Dorney and Watson
- 1978 Zhilinskii and Pavlichenkov
- 1978 Harter and Patterson
- 1991 Lehmann
- 1992 Kozin et al
- 1993 Kozin and Jensen
- 1994 Jensen and Bunker
- 1996 Kozin et al
- 1997 Jensen et al
- 2000 Jensen

2012 Jensen

8-fold and 6-fold clusters CH₄  $H_2O$  4-fold clusters ( $E_{rb}$ ) Rotational energy surfaces and clusters Local mode theory and clusters H<sub>2</sub>Se 4-fold clusters observed  $H_2Se$  4-fold cluster theory ( $E_{rbs}$ ) H<sub>2</sub>X 4-fold cluster symmetry  $H_2Te$  4-fold clusters (exp and theory) Review paper on 4-fold clusters Review paper on LMT and clusters [Mol. Phys. 98, 1253-1285 (2000)] Another review paper on LMT and clusters

[*WIREs Comput. Mol. Sci. (Wiley Interdisciplinary Reviews)* **2**, 494–512 (2012)]



#### H<sub>2</sub>Te Rigid Rotor Energy Levels





#### **Actual H<sub>2</sub>Te Energy Levels**







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 $\Gamma_{\text{Cluster}} = A_1 \oplus A_2 \oplus B_1 \oplus B_2 \quad \text{in} \quad C_{2v}(M)$ 



#### **Programs: XY3 and TROVE**

(Theoretical Rotation-Vibration Energies)

XY3: Rotation-vibration energies for pyramidal, ammonia-type molecule in isolated electronic state, calculated variationally.

[1] H. Lin *et al.*, *J. Chem. Phys.* **117**, 11265 (2002)
[2] S.N. Yurchenko *et al.*, *Mol. Phys.* **103**, 359 (2005) and references given there.

TROVE: Rotation-vibration energies for any molecule in isolated electronic state, calculated variationally.

[3] S.N. Yurchenko, W. Thiel, and P. Jensen, *J. Mol. Spectrosc.* **245**, 126 (2007)



# Variational rotation-vibration calculations for PH<sub>3</sub>

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 $J \leq 80$ 

Vibrational basis set:

$$2(v_1 + v_2 + v_3) + v_{inv} + V_{bend} \le 6$$

**Potential energy surface:** 

cc-pwCVTZ [1] refined by fitting to experimental vibrational term values [2]

[1] D. Wang, Q. Shi, and Q.-S. Zhu, *J. Chem. Phys.*, **112**, 9624 (2000)
[2] S.N. Yurchenko *et al.*, *Chem. Phys.* **290**, 59 (2003)











#### **Watson-type Hamiltonian for PH<sub>3</sub>**



L. Fusina, G. Di Lonardo, J. Mol. Struct. 517-518, 67 (2000)



#### **Rotational coordinates**

xyz is molecule-fixed; XYZ is space-fixed



- $(\theta, \varphi, \chi)$  define orientation of molecule (*xyz*) relative to laboratory (*XYZ*).
- $(\theta, \chi)$  define orientation of Z axis relative to molecule (xyz).



For a rovibronic eigenstate  $\Phi_i$   $F_{J,m}(\theta, \chi) = \int (\Phi_i)^* \Phi_i \sin \theta \, dV$   $\Delta$ Integration over all vibronic coordinates and  $\varphi$ 

is the probability distribution for the orientation of the Z axis relative to the molecule.

 $F_{J,m}(\theta,\chi)$ 





"Top cluster states" for J = m = 40, vibrational ground state of PH<sub>3</sub>



## **Primitive cluster states** $|j PCS \rangle$

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#### First symmetrize, e.g.

$$\Psi_{1}^{A_{1}} = \frac{1}{\sqrt{6}} \left( |1 \text{ PCS}\rangle + |2 \text{ PCS}\rangle + |3 \text{ PCS}\rangle + |4 \text{ PCS}\rangle + |5 \text{ PCS}\rangle + |6 \text{ PCS}\rangle \right)$$
$$\Psi_{6}^{A_{2}} = \frac{1}{\sqrt{6}} \left( |1 \text{ PCS}\rangle + |2 \text{ PCS}\rangle + |3 \text{ PCS}\rangle - |4 \text{ PCS}\rangle - |5 \text{ PCS}\rangle - |6 \text{ PCS}\rangle \right)$$
with similar expressions for the *E* functions....













#### **PH<sub>3</sub> intensity calculations**

*Ab initio* (CCSD(T)/aug-cc-pVTZ) <sup>2</sup> dipole moment surfaces <sup>2</sup>

Rotation-vibration wavefunctions from the variational calculation

Experimental data from L. R. Brown, R. L. Sams, I. Kleiner, C. Cottaz, and L. Sagui, *J. Mol. Spectrosc.* **215**, 178-203 (2002)





#### **PH<sub>3</sub> cluster transitions**

Large line strengths at high *J* 

Can the lower states be populated somehow?







# Similar effects for XHD<sub>2</sub> or XH<sub>2</sub>D molecules?



#### **XH<sub>2</sub>D: Cluster-free molecules**





#### **XHD**<sub>2</sub>: Molecules with rotational energy cluster formation





#### Conclusions

Local mode phenomena manifest themselves as

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- clustering of vibrational energy levels at high vibrational excitation
- clustering of rotation—vibration energy levels at high rotational excitation.

Thus local mode behaviour is induced by both vibrational and rotational excitation.



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