Molecules in highly excited rotational states

\[ J \sim 100 \]
$H_2Te$ Rigid Rotor Energy Levels [$E(J_{kaKc})-E(J_{J0})$]

$J_{J,0}$
$J_{J,1}$
$J_{J-1,1}$
$J_{J-1,2}$
$J_{J-2,2}$
$J_{J-2,3}$
$J_{J-3,3}$
$J_{J-3,4}$
$J_{J-4,4}$

$A_e = 6.26$, $B_e = 6.11$, $C_e = 3.09$ cm$^{-1}$
Actual $\text{H}_2\text{Te}$ Energy Levels $[E(J_{K_aK_c})-E(J_{J0})]$
\[ \Gamma_{\text{Cluster}} = A_1 \oplus A_2 \oplus B_1 \oplus B_2 \quad \text{in} \quad C_{2v}(M) \]
Rotational Energy Level Clusters

1972  Dorney and Watson  CH$_4$  8-fold and 6-fold clusters
1978  Zhilinskii and Pavlichenkov  H$_2$O  4-fold clusters ($E_{rb}$)
1978  Harter and Patterson  Rotational energy surfaces and clusters
1991  Lehmann  Local mode theory and clusters
1992  Kozin et al  H$_2$Se  4-fold clusters observed
1993  Kozin and Jensen  H$_2$Se  4-fold cluster theory ($E_{rbs}$)
1994  Jensen and Bunker  H$_2$X  4-fold cluster symmetry
1996  Kozin et al  H$_2$Te  4-fold clusters (exp and theory)
1997  Jensen et al  Review paper on 4-fold clusters
Are there similar effects for $\text{XH}_3$ molecules – say $\text{PH}_3$?
But first: What do we want to compute here?

-Molecular rotation-vibration energies!

How do we do that?

Solution of the rotation-vibration Schrödinger equation!
Very basic: Nonrelativistic molecular Hamiltonian

(10) \[ \hat{H}(\mathbf{r}, \mathbf{R}) = \hat{T}_N(\mathbf{R}) + \hat{T}_{\text{el}}(\mathbf{r}) + \hat{V}_{\text{Ne}}(\mathbf{r}, \mathbf{R}) + \hat{V}_{\text{ee}}(\mathbf{r}) + \hat{V}_{\text{NN}}(\mathbf{R}) \]

Kinetic energy:

(11) \[ \hat{T}_N(\mathbf{R}) = -\sum_A \frac{\hbar^2}{2M_A} \left(\frac{\partial^2}{\partial x_A^2} + \frac{\partial^2}{\partial y_A^2} + \frac{\partial^2}{\partial z_A^2}\right) = -\sum_A \frac{\hbar^2}{2M_A} \Delta_A \]

(12) \[ \hat{T}_{\text{el}}(\mathbf{r}) = -\frac{\hbar^2}{2m} \sum_i \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}\right) = -\frac{\hbar^2}{2m} \sum_i \Delta_i \]

Potential energy:

(13) \[ \hat{V}_{\text{Ne}}(\mathbf{r}, \mathbf{R}) = -\sum_A \sum_i Z_A e^2 / r_{Ai} \]

(14) \[ \hat{V}_{\text{ee}}(\mathbf{r}) = + \sum_{i<j} \sum e^2 / r_{ij} \]

(15) \[ \hat{V}_{\text{NN}}(\mathbf{R}) = + \sum_{A<B} \sum Z_A Z_B \cdot e^2 / R_{AB} \]
Nonrelativistic molecular Hamiltonian

\[ \hat{\mathcal{H}} \] takes into account the nonrelativistic kinetic energy and the potential energy of the Coulomb interaction.

Neglect of:

- Relativistic corrections of the kinetic energy
- Interactions of magnetic moments (orbit/orbit, spin/orbit, spin/spin)
- Interactions with external electric or magnetic fields
Also very basic: Born-Oppenheimer Approximation

Goal: separation of nuclear motion and electronic motion.

Idea: Electrons are much lighter than nuclei and hence move much faster. They adapt themselves almost instantaneously to each new nuclear configuration.

Approach: The electronic wave function $\Psi_{\text{el}}(\mathbf{r},\mathbf{R})$ is evaluated for a fixed nuclear configuration ($\mathbf{R}$). It depends directly on $\mathbf{r}$ and parametrically on $\mathbf{R}$.

\begin{align}
\hat{H}_{\text{el}}(\mathbf{r},\mathbf{R}) &= \hat{T}_{\text{el}}(\mathbf{r}) + \hat{V}_{\text{Ne}}(\mathbf{r},\mathbf{R}) + \hat{V}_{\text{ee}}(\mathbf{r}) \\
\hat{H}_{\text{el}}(\mathbf{r},\mathbf{R})\Psi_{\text{el}}(\mathbf{r};\mathbf{R}) &= E_{\text{el}}(\mathbf{R})\Psi_{\text{el}}(\mathbf{r};\mathbf{R})
\end{align}

Ab initio calculation!

We sometimes use ab initio calculations with commercially available programs (MOLPRO).

Born-Oppenheimer potential energy
Nuclear-motion calculations

Assuming that vibronic couplings are negligibly small, for every electronic state there is an effective Schrödinger equation to treat nuclear motion:

\begin{align}
(18) \quad & \hat{H}_N(R)\chi_m(R) = E\chi_m(R) \\
(19) \quad & \hat{H}_N(R) = \hat{T}_N(R) + \hat{V}_m^{\text{eff}}(R)
\end{align}

The effective potential energy for the nuclear motion is the Born-Oppenheimer potential energy surface (PES):

\begin{equation}
(20) \quad \hat{V}_m^{\text{eff}}(R) = E_{\text{el}}(R) + V_{NN}(R) = U(R)
\end{equation}

This is what we do in Wuppertal!
And how: By diagonalizing the nuclear Hamiltonian!

Schrödinger equation

\[ \hat{H} \psi_j = E_j \psi_j \]

Eigenvalues and –functions are found by diagonalization of a matrix with elements

\[ \psi_j = \sum_n C_{jn} \psi_n^0 \]

LAPACK, DSYEVX, Profs. Lang and Frommer ...
For PH$_3$ etc: Investigation by variational rotation-vibration calculations

Basis functions:

$$|\Psi_{\text{Basis}}\rangle = |J, K, m\rangle v_{\text{inv}}, J, K \rangle \Psi_{v_1}^{\text{MO}}(\xi_1) \times \Psi_{v_2}^{\text{MO}}(\xi_2) \times \Psi_{v_3}^{\text{MO}}(\xi_3) \times \Psi_{V, l}^{\text{HO}}(\xi_{4a}, \xi_{4b})$$

Rigid rotor eigenfunctions

Morse oscillators

Two-dimensional isotropic harmonic oscillators for doubly degenerate bending vibrations

Hougen-Bunker-Johns theory: Eckart & Sayvetz conditions

$\Rightarrow \hat{T}_{\text{nuc}} = \text{expansion in the } \xi_i$
Programs: XY3 and TROVE
(Theoretical Rotation-Vibration Energies)

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

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


Variational rotation-vibration calculations for PH$_3$

$J \leq 80$

Vibrational basis set:

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

Potential energy surface:

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

Yes, there are six-fold clusters!

\[
\Gamma_{\text{Cluster}} = A_1 \oplus A_2 \oplus 2E \quad \text{in } C_{3v}(M)
\]
\[ |1 \text{ PCS} \rangle = E |1 \text{ PCS} \rangle \]

\[ \Gamma_{\text{Cluster}} = A_1 \oplus A_2 \oplus 2E \text{ in } C_{3v}(M) \]
Watson-type Hamiltonian for PH$_3$

“Cluster spread”, vibrational ground state of PH$_3$

„Critical phenomenon“ here?
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 \( \Phi_i \)

\[
F_{J,m}(\theta, \chi) = \int (\Phi_i)^* \Phi_i \sin \theta \, dV
\]

Integration over all vibronic coordinates and \( \varphi \)

is the probability distribution for the orientation of the \textbf{Z axis} relative to the molecule.
$F_{J,m}(\theta, \chi)$

“Top cluster states” for $J = m = 40$, vibrational ground state of PH$_3$
Primitive cluster states $|j\text{PCS}\rangle$

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....
\[ |1 \text{ PCS} \rangle \]

\[ \theta = 94^\circ \]

\[ F_{J,m=J}(\theta, \chi) = \int (\Phi_i)^* \Phi_i \sin \theta \, dV \]
\[ |1 \text{ PCS} \rangle \]

\[ J = 40 \]

\[ \theta = 98^\circ \]
| 1 PCS ⟩

\[ J = 60 \]

\[ \theta = 108^\circ \]
\[ |1 \text{ PCS} \rangle \quad \theta_{eq} = 123^\circ \]

\[ J = 80 \]

\[ \theta = 113^\circ \]
$|1 \text{ PCS}$

$J=80$
PH$_3$ intensity calculations

*Ab initio* (CCSD(T)/aug-cc-pVTZ) dipole moment surfaces

Rotation-vibration wavefunctions from the variational calculation

**PH$_3$ cluster transitions**

(A)

\[ \begin{align*}
K_c = 0, A_1/A_2 & \\
1, E & \\
2, E & \\
3, A_2/A_1 & \\
3, A_1/A_2 & \\
4, E & \\
5, E & \\
6, A_2/A_1 &
\end{align*} \]

Large line strengths at high $J$

Can the lower states be populated somehow?
Also similar effects for XHD$_2$ or XH$_2$D molecules, say PHD$_2$ or PH$_2$D?
PH$_2$D rotational energies: TROVE calculations

No cluster formation found for PH$_2$D
XH$_2$D: Cluster-free molecules

Reduced rotational term values
PHD$_2$ rotation energies: TROVE calculations

Reduced rotational term values in the vibrational ground state of PHD$_2$
XHD$_2$: Molecules with rotational energy cluster formation

Reduced rotational term values
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