Molecules in highly excited rotational states

$J \sim 100$
H₂Te Rigid Rotor Energy Levels \([E(J_{KaKc})-E(J_{J0})]\)

\[
\begin{align*}
J_{J,0} & \\
J_{J,1} & \\
J_{J-1,1} & \\
J_{J-1,2} & \\
J_{J-2,2} & \\
J_{J-2,3} & \\
J_{J-3,3} & \\
J_{J-3,4} & \\
J_{J-4,4} & \\
\end{align*}
\]

\(A_c=6.26, \quad B_c=6.11, \quad C_c=3.09 \text{ cm}^{-1}\)
Actual H$_2$Te Energy Levels [$E(J_{KaKc})-E(J_{J0})$]
\[
\Gamma_{\text{Cluster}} = A_1 \oplus A_2 \oplus B_1 \oplus B_2 \quad \text{in} \quad C_{2v}(M)
\]
<table>
<thead>
<tr>
<th>Year</th>
<th>Author(s)</th>
<th>Cluster Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1972</td>
<td>Dorney and Watson</td>
<td>CH$_4$ 8-fold and 6-fold clusters</td>
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<tr>
<td>1978</td>
<td>Zhilinskii and Pavlichenkov</td>
<td>H$<em>2$O 4-fold clusters ($E</em>{rb}$)</td>
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<tr>
<td>1978</td>
<td>Harter and Patterson</td>
<td>Rotational energy surfaces and clusters</td>
</tr>
<tr>
<td>1991</td>
<td>Lehmann</td>
<td>Local mode theory and clusters</td>
</tr>
<tr>
<td>1992</td>
<td>Kozin et al</td>
<td>H$_2$Se 4-fold clusters observed</td>
</tr>
<tr>
<td>1993</td>
<td>Kozin and Jensen</td>
<td>H$<em>2$Se 4-fold cluster theory ($E</em>{rbs}$)</td>
</tr>
<tr>
<td>1994</td>
<td>Jensen and Bunker</td>
<td>H$_2$X 4-fold cluster symmetry</td>
</tr>
<tr>
<td>1996</td>
<td>Kozin et al</td>
<td>H$_2$Te 4-fold clusters (exp and theory)</td>
</tr>
<tr>
<td>1997</td>
<td>Jensen et al</td>
<td>Review paper on 4-fold clusters</td>
</tr>
<tr>
<td>2000</td>
<td>Jensen</td>
<td>Review paper on LMT and clusters</td>
</tr>
</tbody>
</table>
Are there similar effects for $\text{XH}_3$ molecules – say $\text{PH}_3$?
Programs: XY3 and TROVE
(Theoretical Rotation-Vibration Energies)

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

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


Variational rotation-vibration calculations for PH$_3$

\[ J \leq 80 \]

Vibrational basis set:

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

Potential energy surface:

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

Yes, there are six-fold clusters!

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

$E_{JK} - E_{J_{\text{max}}}$ / cm$^{-1}$

J =

0 10 20 30 40 50 60 70

0.0

-20.0

-40.0

-60.0

-80.0

-100.0


L. Fusina, G. Di Lonardo,
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 $\Phi_i$,

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

is the probability distribution for the orientation of the $Z$ axis relative to the molecule.
"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....
\[ F_{J,m=J}(\theta, \chi) = \int (\Phi_i)^* \Phi_i \sin \theta \, dV \]
$|1 \text{ PCS} \rangle$

$\theta_{eq} = 123^\circ$

$J=80$

$\theta = 113^\circ$
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

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

Cluster formation for PHD$_2$

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

Reduced rotational term values

![Graph showing rotational energy levels for BiHD$_2$, SbHD$_2$, and PHD$_2$.](image-url)
Thanks & Acknowledgments

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