Energetically Feasible Proton Permutations in the Photodissociation of H$_5^+$

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\[
H_2 + H_3^+ \leftrightarrow [H_2 - H - H_2]^+ \leftrightarrow H_3^+ + H_2
\]

- Large amplitude motions in \(H_5^+ ([H_2 - H - H_2]^+)\) allows protons to permute \(\rightarrow\) open different pathways for the proton transfer reaction.\[1,2,3,4\]

Photodissociation of $\text{H}_5^+ : \text{Two Steps.}$

$$[\text{H}_2 - \text{H} - \text{H}_2]^+ \xrightarrow{+h\nu} ([\text{H}_2 - \text{H} - \text{H}_2]^+)^* \xrightarrow{\text{dissociation}} \text{H}_3^+ + \text{H}_2$$

Questions to Ask

- Feasible proton permutations?
- Symmetry-allowed combinations of states?
- Electric-dipole selection rules?
- Correlation rules?
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Feasible Permutations for \([H_2 - H - H_2]^+\)

- Torsion and proton transfer are allowed.\(^{[1,2,3]}\)

\[ P = (12), (34), (12)(34) \]

\[ \varepsilon_0^{\text{tor}} \approx \frac{1}{2} \Delta_0^{\text{tor}} \]

\[ V(\phi) \]

Feasible Permutations for $[\text{H}_2 - \text{H} - \text{H}_2]^+$

- Torsion and proton transfer are allowed.\cite{Lin,McCoy1,McCoy2,McCoy3}

\[ P = (13)(24), (14)(23) \]
\[ \text{or } P = (1324), (1423) \]
\[ \varepsilon_0^{\text{pt}} > \Delta_0^{\text{pt}} \]

Feasible Permutations for $[\text{H}_2 - \text{H} - \text{H}_2]^+$

- Torsion and proton transfer are allowed.

\[
\begin{bmatrix}
E \\
(12) \\
(34) \\
(12)(34) \\
(13)(24) \\
(14)(23) \\
(1324) \\
(1423)
\end{bmatrix}
\otimes
\begin{bmatrix}
E \\
E^*
\end{bmatrix}
\rightarrow \mathcal{G}_{16}
\]

Feasible Permutations for $\text{H}_3^+ + \text{H}_2$

- Permutations are allowed only within each fragment, $\text{H}_2$ or $\text{H}_3^+$.

$$\left[ P(\text{H}_3^+) \right] \otimes \left[ P(\text{H}_2) \right] \otimes \begin{bmatrix} E \\ E^* \end{bmatrix} \rightarrow G_{24}$$

$$3! \times 2! \times 2 = 24$$

Questions to Ask

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\[ G_{16} + \hbar \nu \]

\[ G_{24} \]

\[ V(R_{\text{diss}}) \text{ (cm}^{-1}) \]

\[ R_{\text{diss}} \text{ (Å)} \]
Questions to Ask

- Feasible proton permutations?
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Rotation/Torsion for \([H_2 - H - H_2]^+\)

- \([H_2 - H - H_2]^+\) includes three coupled rotors.\(^{[1,2]}\)

\[
\begin{align*}
\chi &= \frac{\phi_1 + \phi_2}{2} \\
\gamma &= \frac{\phi_2 - \phi_1}{2} \\
\chi_5 &= \phi_5 - \chi
\end{align*}
\]

- \(\chi_5\) includes \(\phi_5\) plus \(\chi\)
- \(\gamma\) includes \(\phi_2\) minus \(\phi_1\)
- \(\chi_5\) includes \(\phi_5\) minus \(\chi\)

\[
\begin{pmatrix}
\phi_1 \\
\phi_2 \\
\phi_5 \\
\chi \\
\gamma \\
\chi_5
\end{pmatrix}
\] 
\(\rightarrow\) 
\[
\begin{pmatrix}
\phi_1 + 2\pi \\
\phi_2 \\
\phi_5 \\
\chi + \pi \\
\gamma + \pi \\
\chi_5 + \pi
\end{pmatrix}
\]

\[\text{[1] Merer & Watson, } J. \text{ Mole. Spec., 1973, 47, 499} \]
\[\text{[2] Lin, } J. \text{ Mole. Spec., 2016, 324, 36.}\]
Rotation/Torsion for $[\text{H}_2 - \text{H} - \text{H}_2]^+$

- Rotation/torsion wave function is invariant under $E'$.[1,2]

\[ K^{pK}(\chi) \propto |J, K\rangle + p_K(-1)^{J+K}|J, -K\rangle \]
\[ N^p_{\gamma}(\gamma) \propto |N_\gamma\rangle + p_\gamma|-N_\gamma\rangle \]
\[ K^p_{55}(\chi_5) \propto |K_5\rangle + p_5|-K_5\rangle \]
\[ K^{pK} \times N^p_{\gamma} \times K^{p5}_{55} \rightarrow \text{itself} \]
\[ G_{16} \otimes \begin{bmatrix} E \\ E' \end{bmatrix} \rightarrow G_{16}^{(2)} \]

single-valued $\Gamma_S = A/B_{1,2}^+(g,u)$, $E^\pm$
double-valued $\Gamma_D = E_{1,2,g,u}$

\[ \Gamma_S \otimes \Gamma_S = \Gamma_S \]
\[ \Gamma_S \otimes \Gamma_D = \Gamma_D \]
\[ \Gamma_D \otimes \Gamma_D = \Gamma_S \]

Rotation/Torsion for $[\text{H}_2 - \text{H} - \text{H}_2]^+$

- Total rotational/torsional symmetry is single-valued.$^{[1,2]}$

![Diagram](image)

<table>
<thead>
<tr>
<th>$\Gamma$</th>
<th>$K_{PK}^{pK}$</th>
<th>$N_{\gamma}^{pK}$</th>
<th>$K_{5}^{p5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1g}^+$</td>
<td>$0^+, 4^+, \ldots$</td>
<td>$0^+, 4^+, \ldots$</td>
<td>$0^+, 4^+, \ldots$</td>
</tr>
<tr>
<td>$A_{1u}^-$</td>
<td>$-$</td>
<td>$2^-, 6^-, \ldots$</td>
<td>$-$</td>
</tr>
<tr>
<td>$A_{2g}^-$</td>
<td>$0^-, 4^-, \ldots$</td>
<td>$-$</td>
<td>$4^-, 8^-, \ldots$</td>
</tr>
<tr>
<td>$B_{1g}^+$</td>
<td>$2^+, 6^+, \ldots$</td>
<td>$2^+, 6^+, \ldots$</td>
<td>$2^+, 6^+, \ldots$</td>
</tr>
<tr>
<td>$B_{1u}^-$</td>
<td>$-$</td>
<td>$4^-, 8^-, \ldots$</td>
<td>$-$</td>
</tr>
<tr>
<td>$B_{2g}^-$</td>
<td>$2^-, 6^-, \ldots$</td>
<td>$-$</td>
<td>$2^-, 6^-, \ldots$</td>
</tr>
<tr>
<td>$E_1$</td>
<td>$-$</td>
<td>$1^\pm, 3^\pm, \ldots$</td>
<td>$-$</td>
</tr>
<tr>
<td>$E_g$</td>
<td>$1^\pm, 3^\pm, \ldots$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>$E_{u}$</td>
<td>$-$</td>
<td>$-$</td>
<td>$1^\pm, 3^\pm, \ldots$</td>
</tr>
</tbody>
</table>

$^{[1]}$ Merer & Watson, *J. Mole. Spec.*, 1973, 47, 499  
Questions to Ask

• Feasible proton permutations?
• Symmetry-allowed combinations of states?
• Electric-dipole selection rules?
• Correlation rules?

\[
|v, J, K, I\rangle \\
|v', J', K', I'\rangle \\
|v'', J'', K'', I''\rangle
\]
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• Feasible proton permutations?
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\[ G_{16}^{(2)} \]

\[ \psi, J', K', I' \]

\[ \psi'', J'', K'', I'' \]

\[ \mu \]

\[ Z \]

\[ G_{24} \]

\[ V(R_{diss}) \ (\text{cm}^{-1}) \]

\[ R_{diss} \ (\text{Å}) \]
Dipole Selection Rules for \([H_2 - H - H_2]^+\)

- An electric dipole allowed transition requires\(^1,^2\)
  \[
  \hat{\mu}_T = \langle \Psi_{rv}' | \hat{\mu}_Z | \Psi_{rv}'' \rangle \hat{e}_Z \neq 0
  \]
- Decompose into body-fixed axes
  \[
  \hat{\mu}_T = \sum_{\alpha=x,y,z} \langle \Psi_r' | \hat{e}_\alpha \cdot \hat{e}_Z | \Psi_r'' \rangle \langle \Psi_t' | \langle \Psi_5' | \langle \Psi_v' | \hat{\mu}_\alpha | \Psi_v'' \rangle | \Psi_5'' \rangle | \Psi_t'' \rangle \hat{e}_\alpha
  \]

\[
\begin{align*}
\Gamma(\hat{e}_\alpha \cdot \hat{e}_Z) & \subseteq \Gamma_r' \otimes \Gamma_r'' \\
\Gamma(\hat{\mu}_\alpha) & \subseteq (\Gamma_v' \otimes \Gamma_v'') \otimes (\Gamma_5' \otimes \Gamma_5'') \otimes (\Gamma_t' \otimes \Gamma_t'')
\end{align*}
\]

- Parallel transition \((\alpha = z)\)
  \[
  \Gamma(\hat{e}_Z \cdot \hat{e}_Z) = A_{2g}^-, \Gamma(\hat{\mu}_Z) = B_{2u}^+ \rightarrow K, N_\gamma + K_5 \ o/e \ to \ o/e
  \]
- Perpendicular transition \((\alpha = x, y)\)
  \[
  \Gamma(\hat{e}_{x,y} \cdot \hat{e}_Z) = E_g, \Gamma(\hat{\mu}_{x,y}) = E_u \rightarrow K, N_\gamma + K_5 \ o/e \ to \ e/o
  \]

Questions to Ask

- Feasible proton permutations?
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\[
\begin{align*}
G_{16}^{(2)} &\neq 0 \\
G_{24} &\neq 0
\end{align*}
\]
Questions to Ask

- Feasible proton permutations?
- Symmetry-allowed combinations of states?
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Correlation Rules of Wave Functions

• Correlation of the wave functions requires\(^1\),\(^2\),\(^3\)

\[
\langle \Psi \left( \mathcal{G}^{(2)}_{16} \right) | P | \Psi \left( \mathcal{G}_{24} \right) \rangle \neq 0
\]

• Nuclear spin is conserved.

• Correlations between nuclear spin eigenstates are straightforward.

• Correlations between rovibrational wave functions are under investigation.

---

Correlation Rules of Nuclear Spins

<table>
<thead>
<tr>
<th>$I$ ($H_5^+$)</th>
<th>$\Gamma_n$ ($G_{16}^{(2)}$)</th>
<th>$I$ ($H_3^+$)</th>
<th>$I$ ($H_2^+$)</th>
<th>$I$ ($H_5^+$)</th>
<th>$\Gamma_n$ ($G_{24}^{(2)}$)</th>
<th>$I$ ($H_3^+$)</th>
<th>$I$ ($H_2^+$)</th>
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</thead>
<tbody>
<tr>
<td>5/2</td>
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<td>1</td>
<td>1/2</td>
<td>$A_{1g}^+$</td>
<td>3/2</td>
<td>1</td>
</tr>
<tr>
<td>3/2</td>
<td>$A_{1g}^+$</td>
<td>3/2</td>
<td>1</td>
<td>1/2</td>
<td>$A_{1g}^+$</td>
<td>1/2</td>
<td>1</td>
</tr>
<tr>
<td>3/2</td>
<td>$A_{1g}^+$</td>
<td>1/2</td>
<td>1</td>
<td>1/2</td>
<td>$B_{1g}^+$</td>
<td>1/2</td>
<td>0</td>
</tr>
<tr>
<td>3/2</td>
<td>$B_{2u}^+$</td>
<td>3/2</td>
<td>1</td>
<td>1/2</td>
<td>$B_{2u}^+$</td>
<td>1/2</td>
<td>1</td>
</tr>
<tr>
<td>3/2</td>
<td>$B_{2u}^+$</td>
<td>1/2</td>
<td>1</td>
<td>1/2</td>
<td>$B_{2u}^+$</td>
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<tr>
<td>3/2</td>
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<td>3/2</td>
<td>0</td>
<td>1/2</td>
<td>$E^+$</td>
<td>1/2</td>
<td>1</td>
</tr>
<tr>
<td>3/2</td>
<td>$E^+$</td>
<td>1/2</td>
<td>1</td>
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<td>$E^+$</td>
<td>1/2</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>species</th>
<th>$I$</th>
<th>species</th>
<th>$I$</th>
<th>species</th>
<th>$I$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$ortho\cdot H_5^+$</td>
<td>5/2</td>
<td>$ortho\cdot H_3^+$</td>
<td>3/2</td>
<td>$ortho\cdot H_3^+$</td>
<td>3/2</td>
</tr>
<tr>
<td>$meta\cdot H_5^+$</td>
<td>3/2</td>
<td>$para\cdot H_3^+$</td>
<td>1/2</td>
<td>$para\cdot H_3^+$</td>
<td>1/2</td>
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<tr>
<td>$para\cdot H_5^+$</td>
<td>1/2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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\[ \langle v, J, K, I(G_{24}) | v', J', K', I' (G_{16}^{(2)}) \rangle \neq 0 \]

\[ \langle v', J', K', I' (G_{16}^{(2)}) | \hat{\mu}_Z | v'', J'', K'', I'' (G_{16}^{(2)}) \rangle \neq 0 \]
Conclusions

• Different geometries different feasible permutations and different permutation-inversion groups.

• Near the equilibrium structure, the rotational-torsional wave function is invariant under $E'$ operation.

• Parallel dipole transition do not affect odd/even of rotational quantum numbers $K$, but perpendicular transitions do.

• Correlation rules between two extreme geometries can be easily determined for nuclear spins.
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