Research supported by the Natural Sciences and Engineering Research Council of Canada.

Departments of Chemistry and Physics, University of Waterloo

Ali Reza Shavaesteh,† Jouli E. Cordono,† and Peter F. Bernath†
Robert J. Le Roy,‡ Dominique R.T. Appadoo,‡ Kevin Anderson,‡

*The A\textsuperscript{1\Xi\gamma} State of AgH

on an Irregular Electronic State: Imposing a Mechanical Model
Background

To be significant, were ignored in most previous analyses.

Diabatic and non-diabatic Born-Oppenheimer breakdown (B0B) effects, which are expected

For both states:

Modern diode laser, FTIR and MW experiments accurately define properties of the lower levels

... that the irregularities of the spectrum, in both position and intensity, may be best explained in terms of an anomalous rotation potential curve and its associated rotation-including potentials.

In 1962 Learner challenged the Cerio-Schmidt interpretation and argued

B[1/2]+ state

In 1943 Cerio and Schmidt assigned that irregular behavior to homonuclear perturbations by

and/or highly perturbed.

Since its first observation, it has been clear that the A[1/2]+ state of NH is highly irregular
with an unusually shape ... or due to perturbations.

However ... we still don't know whether the A-state level

to be significant, were ignored in most previous analyses.

Adiabatic and non-adiabatic Born-Oppenheimer breakdown (BOB) effects, which are expected

for both states.

Modern close laser, FTIR and NW experiments accurately define properties of the lower levels.

potential curve and its associated rotation-including potentials.

the irregularities of the spectrum, in both position and in-

In 1962 Learner challenged the Gerl-Schmidt interpretation and argued

the nearby $B^{1}Σ_{g}^{+}$ state.

In 1973 Gerl and Schmidt assigned that irregular behavior to homogeneous perturbations by

and/or highly perturbed.

Since its first observation, it has been clear that the $A^{1}Σ_{g}^{+}$ state of $AH$ is highly irregular.

Background
What else is known?
\[ D^gA (0 = ^A\Lambda) + Z^1 X^+ Z^1 V \]

\[ H^gA (0 = ^A\Lambda) + Z^1 X^+ Z^1 V \]
which suggests …

… the same (mass-scaled) curve and $\Delta G$ (square points) fall on results for $\Delta H$ (round points) …

… however, unusual $\nu$-dependence; those for the $A$ state show …

… but very smoothly and relatively $^{a}B \propto \zeta/\Gamma^{a}C \Delta$.

From a preliminary analysis …
2. Fixing the X-state, examine increasingly sophisticated models for the A state.

1. Determine a complete description of the X state while making no assumptions about the nature of the A state.

How shall we proceed?

radial potential defined by some effective "mechanical" model with levels which suggests that the A-state might be...

... the same (mass-scaled) curve and all data (square points) fall on results for \( \text{AgH} \) (round points)...

However, unusual sensitivity of...

... but verify smoothly and regularly...

From a preliminary analysis
Translated: How do we represent the data?
\[ \frac{d^2 H + dH}{d^2 H - dH} = (H)^{dH} = \frac{dH}{\partial H} \\]
where
\[ 2 \left[ (\frac{d^2 H - dH}{d^2 H + dH}) - \frac{dH}{\partial H} - 1 \right] \varphi = (H)^{dH} \\]

[Table and diagram with values and annotations]
so the MLJ² function is best. 

Approximately from below, 

\[ [(\nu)^d \Lambda - \nu \text{C}] \times \nu \text{H} \]

But for a MLJ² potential

\[ \frac{\nu}{\nu \text{C}} = \nu \text{C} \approx \]

\[ \frac{\text{d}^{\nu} \text{H} \text{d} \nu}{\text{d} \nu \text{H} \text{d} \nu} = (\nu)^d \text{H} = d \text{H} \]

where

\[ \left[ (\nu)^d \text{H} \text{d} \nu \text{C} \Lambda \right] \text{C} = (\nu)^d \text{H} \alpha \]

<table>
<thead>
<tr>
<th>MLJ² potential: 19300 (±6.9)</th>
<th>19000 (±6.9)</th>
<th>18700 (±6.9)</th>
<th>18400 (±6.9)</th>
<th>18100 (±6.9)</th>
<th>17800 (±6.9)</th>
<th>17500 (±6.9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00 0.02 0.04 0.06 0.08 0.1</td>
<td>0.00 0.02 0.04 0.06 0.08 0.1</td>
<td>0.00 0.02 0.04 0.06 0.08 0.1</td>
<td>0.00 0.02 0.04 0.06 0.08 0.1</td>
<td>0.00 0.02 0.04 0.06 0.08 0.1</td>
<td>0.00 0.02 0.04 0.06 0.08 0.1</td>
<td>0.00 0.02 0.04 0.06 0.08 0.1</td>
</tr>
<tr>
<td>MLJ² potential: 19334 (±7.2)</td>
<td>19158 (±7.2)</td>
<td>18982 (±7.2)</td>
<td>18806 (±7.2)</td>
<td>18630 (±7.2)</td>
<td>18454 (±7.2)</td>
<td>18278 (±7.2)</td>
</tr>
<tr>
<td>MLJ² potential: 19329 (±7.1)</td>
<td>19153 (±7.1)</td>
<td>18977 (±7.1)</td>
<td>18801 (±7.1)</td>
<td>18625 (±7.1)</td>
<td>18449 (±7.1)</td>
<td>18273 (±7.1)</td>
</tr>
<tr>
<td>MLJ² potential: 19328 (±7.1)</td>
<td>19152 (±7.1)</td>
<td>18976 (±7.1)</td>
<td>18800 (±7.1)</td>
<td>18624 (±7.1)</td>
<td>18448 (±7.1)</td>
<td>18272 (±7.1)</td>
</tr>
<tr>
<td>MLJ² potential: 19329 (±7.1)</td>
<td>19153 (±7.1)</td>
<td>18977 (±7.1)</td>
<td>18801 (±7.1)</td>
<td>18625 (±7.1)</td>
<td>18449 (±7.1)</td>
<td>18273 (±7.1)</td>
</tr>
<tr>
<td>MLJ² potential: 19329 (±7.1)</td>
<td>19153 (±7.1)</td>
<td>18977 (±7.1)</td>
<td>18801 (±7.1)</td>
<td>18625 (±7.1)</td>
<td>18449 (±7.1)</td>
<td>18273 (±7.1)</td>
</tr>
<tr>
<td>MLJ² potential: 19329 (±7.1)</td>
<td>19153 (±7.1)</td>
<td>18977 (±7.1)</td>
<td>18801 (±7.1)</td>
<td>18625 (±7.1)</td>
<td>18449 (±7.1)</td>
<td>18273 (±7.1)</td>
</tr>
</tbody>
</table>

First fit to the X-state alone

While representing X-state levels by term values
<table>
<thead>
<tr>
<th>( \alpha )</th>
<th>( \beta )</th>
<th>( \gamma )</th>
<th>( \delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.15</td>
<td>1.82</td>
<td>1.3</td>
<td>31</td>
</tr>
<tr>
<td>(942)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.91</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Using our 31-parameter model for the X-state, both states simultaneously...
<table>
<thead>
<tr>
<th>1/2 - 1/2</th>
<th>( \frac{3}{2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

- Dumbbell parameter: all Dumbbell parameters
- 31 Dumbbell parameter
- 31 Dumbbell parameter
- 31 Dumbbell parameter
- 31 Dumbbell parameter
- 31 Dumbbell parameter
- 31 Dumbbell parameter
- 31 Dumbbell parameter
- 31 Dumbbell parameter
- 31 Dumbbell parameter
- 31 Dumbbell parameter
- 31 Dumbbell parameter
- 31 Dumbbell parameter
- 31 Dumbbell parameter
- 31 Dumbbell parameter
- 31 Dumbbell parameter
- 31 Dumbbell parameter

- All Dumbbell parameters: 64 \( \chi \) and 30 BOP parameters
- All Dumbbell parameters
- All Dumbbell parameters
- All Dumbbell parameters
- All Dumbbell parameters
- All Dumbbell parameters
- All Dumbbell parameters
- All Dumbbell parameters
- All Dumbbell parameters
- All Dumbbell parameters
- All Dumbbell parameters
- All Dumbbell parameters
- All Dumbbell parameters
- All Dumbbell parameters
- All Dumbbell parameters
- All Dumbbell parameters
- All Dumbbell parameters

Using our 31 parameter

Dumbbell model for the \( X \)-state:

**Note:** "parameter" plus to
Dunham model for the $X$-state.

Using our 3J-parameter, both states simultaneously fit to parameter "perturbation", in that the $A$ state may have an irregular shape, but it is not "perturbed".

This suggests:

Dunham model for the $X$-state.

All Dunham: 64 $\nu_{1\alpha}$ and 30 BOB parameters. Dunham for $C^*$ $B$ plus CDC band constants. Dunham for $C^*$ plus rotational band constants all Dunham parameters. Dunham for $C^*$ plus rotational band constants.

$\nu_{1\alpha}$ values $L(\nu)_{\alpha}$

- State model

$pp$ $N$ $X$-state model

no. param.
Finally... direct potential fits to both states simultaneously!
radial correction functions.

adiabatic & non-adiabatic effective radial potential plus spacings are explained by an "mechanical" since its level

The A_{1}X_{1} state of AgH is

Conclude

to both states simultaneously!

\[ \begin{array}{cccc}
\text{MLJ}^{\text{v}} (8,8) & \text{EMO}^{\text{v}} (4,10) & 40 & 1.45 \\
\text{MLJ}^{\text{v}} (8,8) & \text{EMO}^{\text{v}} (4,9) & 39 & 1.53 \\
\text{Dunham} & \text{Dunham} & 1.25 & 1.13 \\
\text{Dunham} & \text{Dunham} & 0.97 & 0.94 \\
\text{Dunham} & \text{Dunham} & 0.97 & 0.94 \\
\end{array} \]