Accurate wavenumber measurements of vibration-rotation transitions of $^{36}\text{ArH}^+$ and $^{38}\text{ArH}^+$

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Motivation:

J=1-0 → 617.5 GHz,  J=2-1 → 1234.6 GHz. Bad atmospheric transmission, even for ALMA

As an alternative, after the end of the Herschel mission, future observations may be carried out in the infrared.
Antecedents

- $^{36}\text{Ar}$ is the most abundant isotope in space.
- On Earth: $^{40}\text{Ar}$ 99.600%, $^{36}\text{Ar}$ 0.337%, $^{38}\text{Ar}$ 0.063%. On Earth $^{40}\text{Ar}$ is produced mainly by $\beta$-decay from $^{40}\text{K}$, and marginally from $^{40}\text{Ca}$.
- Previous spectroscopic work:

<table>
<thead>
<tr>
<th>Pure rotation</th>
<th>Vibration-rotation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bowman et al</td>
<td>J=1-0</td>
</tr>
<tr>
<td>Liu, Ho, Oka</td>
<td></td>
</tr>
<tr>
<td>Laughlin et al</td>
<td></td>
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<tr>
<td>Brown et al</td>
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<tr>
<td>Odashima et al</td>
<td></td>
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<tr>
<td>Brault &amp; Davis</td>
<td></td>
</tr>
<tr>
<td>Johns</td>
<td></td>
</tr>
<tr>
<td>Haese &amp; Oka</td>
<td></td>
</tr>
<tr>
<td>Filgueira &amp; Blom</td>
<td></td>
</tr>
<tr>
<td>This work</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE I**

Experimental and Predicted Line Positions for $^{36}\text{ArH}^+$ and $^{38}\text{ArH}^+$

<table>
<thead>
<tr>
<th>Line</th>
<th>$^{36}\text{ArH}^+$</th>
<th>$^{38}\text{ArH}^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>observed</td>
<td>o-c</td>
</tr>
<tr>
<td>R(3)</td>
<td>2667.414</td>
<td>0.000</td>
</tr>
<tr>
<td>R(2)</td>
<td>2649.896</td>
<td>-0.001</td>
</tr>
<tr>
<td>R(1)</td>
<td>2631.589</td>
<td>+0.001</td>
</tr>
<tr>
<td>P(2)</td>
<td>2550.720</td>
<td>-0.001</td>
</tr>
<tr>
<td>P(3)</td>
<td>2528.672</td>
<td>+0.001</td>
</tr>
<tr>
<td>P(4)</td>
<td>2505.918</td>
<td>+0.001</td>
</tr>
</tbody>
</table>

- Rather good predictions can be made both in rotation and vibration-rotation (CDMS, MADEX, ...)

Cueto, Cernicharo, Tanarro, Herrero, Domenech, ISMS Urbana IL 2014, TF03
ACCURATE LABORATORY MEASUREMENTS OF VIBRATION-ROTATION TRANSITIONS OF $^{36}\text{ArH}^+$ and $^{38}\text{ArH}^+$
Difference frequency spectrometer

- $I_2$ locked Ar$^+$ laser & Ring dye laser
- Mixing in LiNbO$_3$ (DFG)
- Spectral purity: $\sim 1 \times 10^8$ (2 MHz)
- Tunability 2.2 – 4.2 $\mu$m (2300-4500 cm$^{-1}$)
- 1.2 cm$^{-1}$ continuous scan
- Sensitivity: $\sim 1 \times 10^4$ (in transmission)
- 10 $\mu$W vs. $10^{-5}$ $\mu$W NEP of InSb
- First setup: Alan Pine (JOSA1976)
- Accuracy: $\sim 3$ MHz (1$\sigma$)
- Wavemeter for the dye laser.

- At each datapoint in the spectrum, we have an ‘instantaneous’ wavemeter reading. The wavemeter is calibrated with the Ar$^+$ laser.
- We can average a lot of scans.
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The discharge cell

- Hollow-cathode discharge
- Design Foster & McKellar
- 250 V rms, 375 mA rms
- White cell, ~22 m inside the cathode
- Current modulated at 3.09 kHz
- IR modulated at 23.19 kHz
- Lock-in detection at 26.28 kHz
- Water cooled.
- Autobalanced subtractive amplifier (Lindsay, 2001)

Precursors:
- Ar (natural isotopic composition) and no $H_2$

Total pressure ~0.4 mbar
Experimental results

- **S/N ~1100** in R(6) \(^{40}\text{ArH}^+\)

- From the linewidth: \(T_{\text{kin}} \approx 380\text{-}400\ \text{K} \approx T_{\text{rot}}\)

- From the ratio of intensities in v=1-0 and v=2-1, \(T_{\text{vib}} \approx 580\ \text{K}\)

- From the transition dipole moment and HW factors, \(N\left[^{40}\text{ArH}^+\right] \approx 4 \times 10^{10} \text{ cm}^{-3}\)
## Results

### Table 1
Observed Line Centers, Their Estimated 1σ Uncertainties, and Spectroscopic Constants of $^{36}$ArH$^+$

<table>
<thead>
<tr>
<th>Isotopologue</th>
<th>Line</th>
<th>$v_{\text{obs}}$ (cm$^{-1}$)</th>
<th>$\sigma$ a</th>
<th>$(O - C)$ b</th>
<th>Constant$^c$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{36}$ArH$^+$</td>
<td>$P(6)$</td>
<td>2458.36336</td>
<td>11.4</td>
<td>0.3</td>
<td>$B_0$ 10.30044364(778)</td>
</tr>
<tr>
<td></td>
<td>$P(5)$</td>
<td>2482.47613</td>
<td>11.3</td>
<td>-5.5</td>
<td>$D_0$ 6.21374(154) × 10$^{-4}$</td>
</tr>
<tr>
<td></td>
<td>$P(4)$</td>
<td>2505.91727</td>
<td>10.5</td>
<td>7.7</td>
<td>$\nu_1$ 2592.651339(42)</td>
</tr>
<tr>
<td></td>
<td>$P(3)$</td>
<td>2528.67068</td>
<td>11.6</td>
<td>3.8</td>
<td>$B_1$ 9.92620133(616)</td>
</tr>
<tr>
<td></td>
<td>$P(2)$</td>
<td>2550.72091</td>
<td>11.8</td>
<td>-8.9</td>
<td>$D_1$ 6.127689(908) × 10$^{-4}$</td>
</tr>
<tr>
<td></td>
<td>$P(1)$</td>
<td>2572.05291</td>
<td>13.2</td>
<td>-2.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$R(0)$</td>
<td>2612.50135</td>
<td>11.3</td>
<td>5.9</td>
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<tr>
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<td>$R(1)$</td>
<td>2631.58798</td>
<td>11.1</td>
<td>-10.6</td>
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<td>$R(2)$</td>
<td>2649.89731</td>
<td>10.3</td>
<td>8.6</td>
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<tr>
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<td>$R(3)$</td>
<td>2667.41441</td>
<td>10.4</td>
<td>-0.3</td>
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<td>$R(4)$</td>
<td>2684.12561</td>
<td>11.9</td>
<td>4.6</td>
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<tr>
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<td>$R(5)$</td>
<td>2700.01671</td>
<td>11.4</td>
<td>-8.8</td>
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<tr>
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<td>$R(6)$</td>
<td>2715.07445</td>
<td>11.3</td>
<td>0.9</td>
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<tr>
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<td>$R(7)$</td>
<td>2729.28504</td>
<td>11.0</td>
<td>2.0</td>
<td></td>
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<td>$^{38}$ArH$^+$</td>
<td>$R(0)$</td>
<td>2610.70177</td>
<td>13.9</td>
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<td>$R(1)$</td>
<td>2629.76268</td>
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<td>$R(2)$</td>
<td>2648.04731</td>
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<td>$R(3)$</td>
<td>2665.54197</td>
<td>14.9</td>
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<tr>
<td></td>
<td>$R(4)$</td>
<td>2682.23225</td>
<td>13.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Notes.**

a $\sigma$ = estimated uncertainty/10$^{-5}$ cm$^{-1}$.

b $(O - C) = (v_{\text{obs}} - v_{\text{calc}})/10^{-5}$ cm$^{-1}$.

c Numbers in parentheses are one standard deviation in units of the last quoted digit, as derived from the fit.
Results

For $^{36}\text{ArH}^+$,

$J(1-0)=617524.4\pm1.2$ MHz (from just our polynomial fit) vs.

$J(1-0)=617525.23\pm0.45$ MHz (Cologne database from a global fit to all previously available data)

We have used our new wavenumbers in a similar fit to all available data using a Dunham type expansion:

$$E(v, J) = \sum_{kl} \mu^{-(k/2+l)} \times U_{kl} \times \left( 1 + \frac{m_e \Delta_{kl}^{\text{Ar}}}{M_{\text{Ar}}} + \frac{m_e \Delta_{kl}^{\text{H}}}{M_{\text{H}}} \right) \times \left( v + \frac{1}{2} \right)^k \times [J(J+1)]^l$$

For $\text{ArH}^+$

$$\mu = \frac{M_{\text{Ar}}M_{\text{H}}}{M_{\text{Ar}} + M_{\text{H}} - m_e}$$

( Watson, JMS 80, 411 (1980))
Results

• Full results from the fit are in Cueto et al. Astrophysical Journal Letters 783, L5 (2014)
• 367 experimental weighted data.
• Different versions of the reduced mass give significantly different quality fits:

\[ \mu = \frac{M_{\text{Ar}} M_{\text{H}}}{M_{\text{Ar}} + M_{\text{H}} - m_e} \]
\[ \sigma_w = 0.82 \]  

\[ \mu = \frac{(M_{\text{Ar}} - m_e) M_{\text{H}}}{M_{\text{Ar}} + M_{\text{H}} - m_e} \]
\[ \sigma_w = 0.72 \]  

\[ \mu = \frac{(M_{\text{Ar}} - m_e/2)(M_{\text{H}} - m_e/2)}{M_{\text{Ar}} + M_{\text{H}} - m_e} \]
\[ \sigma_w = 0.76 \]  

\[ \mu = \frac{M_{\text{Ar}} M_{\text{H}}}{M_{\text{Ar}} + M_{\text{H}}} \]
\[ \sigma_w = 0.72 \]

• We have used ② as the charge modified reduced mass; i.e. all the charge is concentrated in the Ar nucleus.
• Standard deviation before the new data \( \sigma = 52.5 \text{ MHz} \)
• Adding our new 19 measurements \( \sigma = 50.7 \text{ MHz} \)
  (only 19 new frequencies and of less accuracy than sub-mm)
Ion kinetics in Ar/H\textsubscript{2} plasmas

We have studied hollow cathode discharges at 2 different pressures and with H\textsubscript{2} fractions from 0 to 100 %

**sources:**

- Ar\textsuperscript{+} + H\textsubscript{2} → ArH\textsuperscript{+} + H
- Ar + H\textsubscript{3}\textsuperscript{+} → ArH\textsuperscript{+} + H\textsubscript{2}
- Ar + e\textsuperscript{-} → Ar\textsuperscript{+} + 2e\textsuperscript{-}

**sinks:**

- ArH\textsuperscript{+} + H\textsubscript{2} → Ar + H\textsubscript{3}\textsuperscript{+}
- ArH\textsuperscript{+} + wall → Ar + H

Similarly to the diffuse interstellar medium, too much H\textsubscript{2} destroys ArH\textsuperscript{+}

In our cathode, when the discharge is on, H\textsubscript{2} is ejected from the cathode. (0.002 mbar H\textsubscript{2} from 0.4 mbar Ar)
Summary

• We have provided direct accurate wavenumbers for 19 vibration-rotation lines of $^{36}$ArH$^+$ and $^{38}$ArH$^+$ (only 8 (6) had been reported before, with much less accuracy)

• This new wavenumbers have improved a Dunham-type fit to all published data ($U_{10}$, $U_{12}$ and $\Delta_{\text{Ar} 10}$ uncertainties decrease by factors 1.8, 1.4, 5.6)

• ArH$^+$ should be detectable in dark clouds at $T < 100$ K against bright IR sources as an IR absorption for column densities $10^{13}$ cm$^{-2}$

• Or in emission if $T_{\text{kin}} > 1000$ K (like possibly in the knots of the Crab nebula)

THANK YOU FOR YOUR ATTENTION
Dear José Luis,

Thanks a lot for your request.
I am the saleswoman in charge of Spain.

The price of 36Ar for 5L is 13000 EUR at least.
I can inquire to our manufacturer for 50-500L this is a huge quote !!

Do you have the budget for this ?

Please keep me informed about your decision.
Have a nice day.
Kind regards,