Millimeter-Submillimeter Spectrum of Van der Waals Bound Ar–H_2O Dimer

Luyao Zou and Susanna L. Widicus Weaver

Department of Chemistry, Emory University
1515 Dickey Dr., Atlanta, GA 30322

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HO_3 Side Product

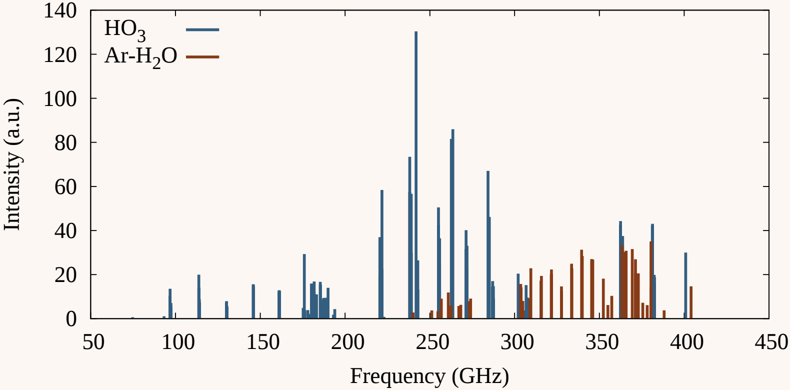

Fig. 1: Millimeter spectrum of HO_3 (blue) with Ar–H_2O lines (brown) as a side product.*

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*L. Zou, B. M. Hays and S. L. Widicus Weaver, *J. Phys. Chem. A*, 2016

Ar–H_2O Submillimeter Spectrum

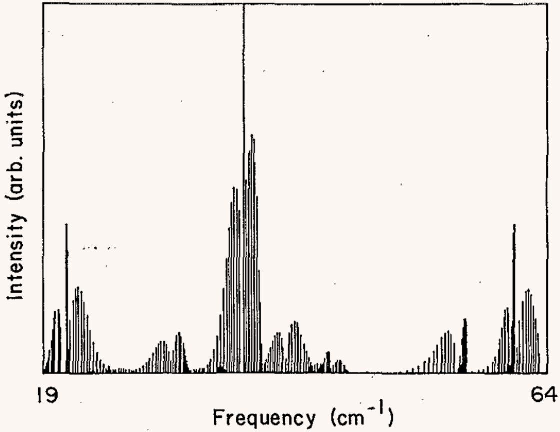


Fig. 2: Submillimeter (0.57–1.92 THz) Spectrum of Ar–H_2O*.

*R. C. Cohen and R. J. Saykally, *J. Chem. Phys.*, 1991

Ar–H_2O free-rotor model

- j_{k_a,k_c}: Rotational QN for H_2O, free rotor
- J: Rotational QN for the dimer, pseudo-diatomic
- Ω: Projection of j on the pseudodiatomic intermolecular axis
  $\Omega = 0, 1, 2, \ldots \Rightarrow \Sigma, \Pi, \Delta, \ldots$
- Coriolis interaction perturbs Σ and Π levels with the same symmetry and in the same j_{k_a,k_c} state.

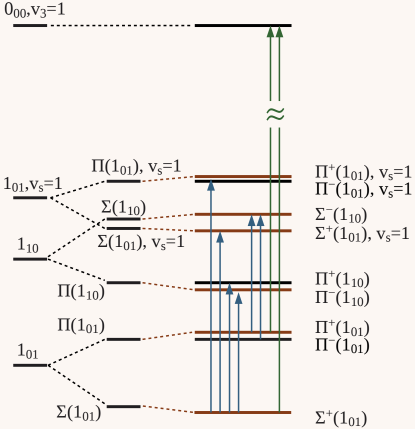


Fig. 3: Ar–H_2O energy diagram.

Ar–H_2O free-rotor model*

- Pseudo-diatomic rotor energy of the dimer:

$$E = v + B\left[J(J+1) - 2\Omega^2\right] - D\left[J(J+1) - 2\Omega^2\right]^2 \tag{1}$$

$$+ H\left[J(J+1) - 2\Omega^2\right]^3 + L\left[J(J+1) - 2\Omega^2\right]^4 \tag{2}$$

- 1^{st}–order Coriolis splitting:

$$E' \approx E \pm 4\beta^2 J(J+1)/(\Delta E) \tag{3}$$

*R. C. Cohen and R. J. Saykally, *J. Chem. Phys.*, 1991

Motivation of This Work

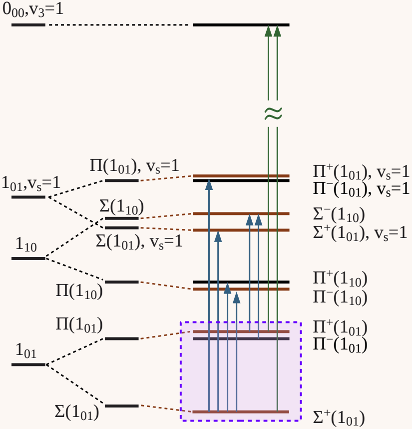


Table 1: Centrifugal distortion constant*

	D (kHz)	H (Hz)
$\Pi^+(1_{01})$	135.49(40)	—
$\Pi^-(1_{01})$	114.76(35)	—
$\Pi^+(1_{10})$	60.44(13)	-21.45(28)
$\Pi^-(1_{10})$	51.42(14)	-12.38(32)

*R. C. Cohen and R. J. Saykally, *J. Chem. Phys.*, 1991

Experimental Setup

- Supersonic expansion. Ar bubbles through water at 24 psi backing pressure.
- Millimeter-submillimeter multipass direct absorption spectrometer.

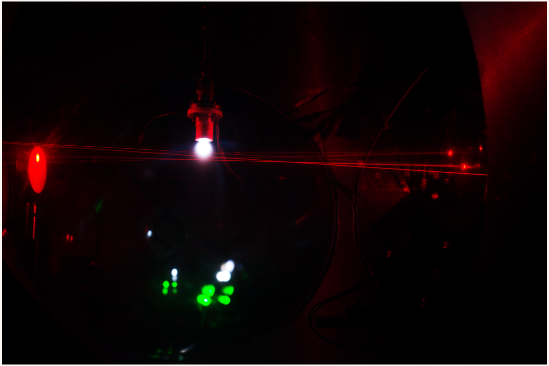


Fig. 4: Picture of the experimental chamber. HeNe laser shows the mm-submm beam path, and CO discharge glow shows the free-jet cone.

Spectrum of Ar–H_2O

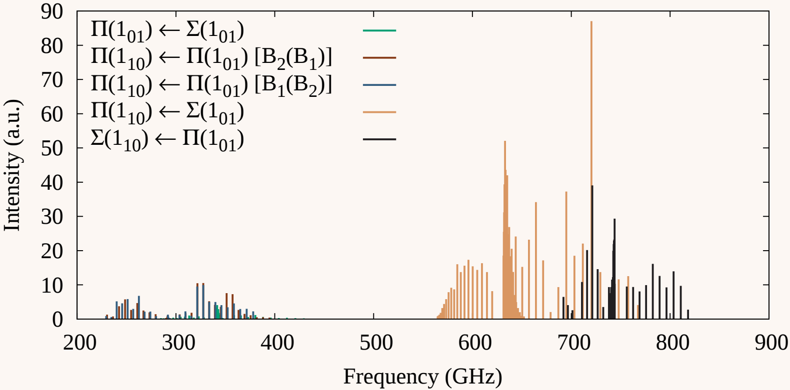


Fig. 5: Millimeter Spectrum of Ar–H_2O *

*L. Zou and S. L. Widicus Weaver, *J. Mol. Spectrosc.*, 2016

Spectrum of Ar–H_2O

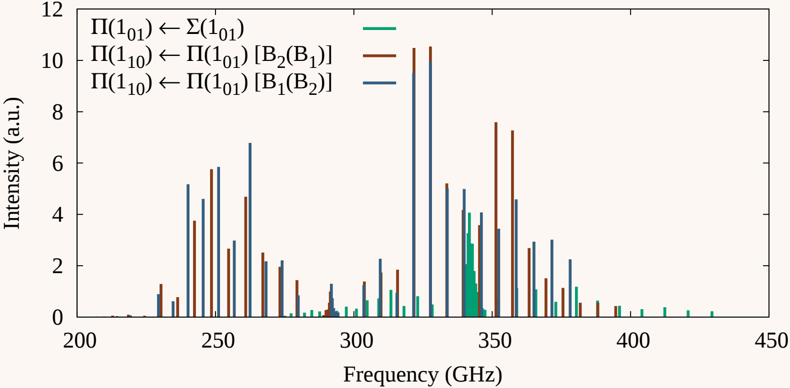


Fig. 5: Millimeter Spectrum of Ar–H_2O *

*L. Zou and S. L. Widicus Weaver, *J. Mol. Spectrosc.*, 2016

Detected Bands

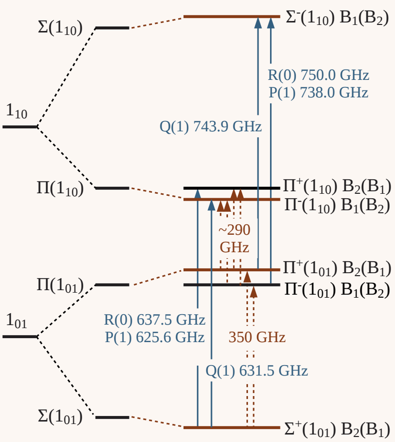
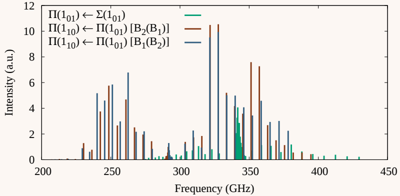


Fig. 6: Ar–H_2O energy diagram.
Arrows: Cohen et al.*; this work†.



- Direct Measurement of millimeter bands

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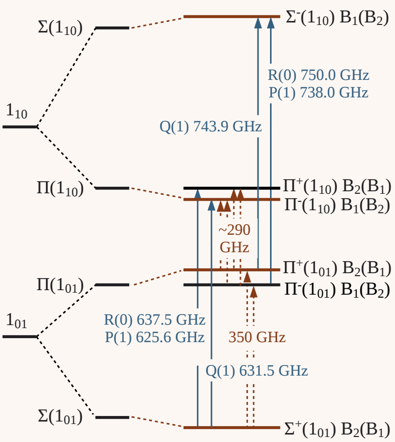

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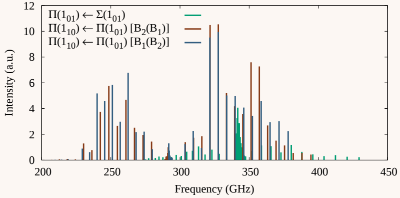

- Direct Measurement of millimeter bands
- Refined Coriolis Interaction

*R. C. Cohen and R. J. Saykally, *J. Chem. Phys.*, 1991

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Analytical Treatment of Coriolis Interaction

$$\text{Coriolis Matrix} = \begin{bmatrix} E_1 & 2\beta\sqrt{J(J+1)} \\ 2\beta\sqrt{J(J+1)} & E_2 \end{bmatrix} \tag{4}$$

Approximate Solution

$$\begin{aligned} E_1' &\approx E_1 - 4\beta^2 J(J+1)/(E_2 - E_1) \\ E_2' &\approx E_2 + 4\beta^2 J(J+1)/(E_2 - E_1) \end{aligned} \tag{5}$$

Analytical Solution

$$\begin{aligned} E_1' &= \frac{1}{2}\left[E_1 + E_2 - (E_2 - E_1)\sqrt{1 + 16J(J+1)\left(\frac{\beta}{E_2 - E_1}\right)^2}\right] \\ E_2' &= \frac{1}{2}\left[E_1 + E_2 + (E_2 - E_1)\sqrt{1 + 16J(J+1)\left(\frac{\beta}{E_2 - E_1}\right)^2)}\right] \end{aligned} \tag{6}$$

Fit Results

Table 2: Molecular constants fitted to Ar–H_2O $j = 1$ *ortho* states

	This Work	Cohen and Saykally*
ν (GHz)†		
$\Sigma(1_{01})$	0	0
$\Pi(1_{01})$	345.590524(18)	345.587(18)
$\Pi(1_{10})$	637.466766(17)	637.46708(43)
$\Sigma(1_{10})$	1083.637495(35)	1083.634(18)
B (MHz)		
$\Sigma(1_{01})$	3014.7865(17)	3014.783(27)
$\Pi(1_{01})$	2951.6969(70)	2951.658(57)
$\Pi(1_{10})$	3037.4887(13)	3037.476(15)
$\Sigma(1_{10})$	2953.1776(31)	2953.224(66)
β (MHz)		
$\Sigma(1_{01}) \leftrightarrow \Pi(1_{01})$	2976.455(14)	2950.84(40)
$\Pi(1_{10}) \leftrightarrow \Sigma(1_{10})$	2862.862(17)	2880.78(33)
r.m.s (MHz)	0.060	0.623

*R. C. Cohen and R. J. Saykally, *J. Chem. Phys.*, 1991

†The band head frequency is model dependent.

Fit Results

Table 3: Molecular constants fitted to Ar–H_2O $j = 1$ *ortho* states

	This Work	Cohen and Saykally*	Diff.
D (kHz)			
$\Sigma^+(1_{01})^\dagger$	90.956(13)	72.616(71)	18.340
$\Pi^+(1_{01})^\dagger$	115.713(20)	135.49(40)	−19.777
$\Pi^-(1_{01})$	114.8240(23)	114.76(35)	0.064
$\Pi^+(1_{10})$	60.824(17)	60.44(13)	0.384
$\Pi^-(1_{10})^\dagger$	65.149(14)	51.42(14)	13.729
$\Sigma^-(1_{10})^\dagger$	98.107(76)	111.75(66)	−13.643
H (Hz)			
$\Sigma^+(1_{01})^\dagger$	−4.316(61)	1.25(20)	−5.556
$\Pi^+(1_{01})^\dagger$	−1.90(13)	—	−1.90
$\Pi^+(1_{10})$	−18.796(92)	−21.45(28)	2.654
$\Pi^-(1_{10})^\dagger$	−18.449(71)	−12.38(32)	−6.069
$\Sigma^-(1_{10})^\dagger$	−14.97(67)	−23.9(22)	8.93

*R. C. Cohen and R. J. Saykally, *J. Chem. Phys.*, 1991

†Coriolis perturbed states.

Conclusion

- 3 new measured millimeter bands
- Band head of $\Pi(1_{01}) \leftarrow \Sigma(1_{01})$
- 2 submillimeter bands with higher frequency resolution
- Spectral assignment and fit with free-rotor model and analytical treatment of the Coriolis interaction
- The centrifugal distortion constants of perturbed/unperturbed Π states are similar after the removal of the contamination from 1^{st}–order approximation of the Coriolis interaction.

Acknowledgement

- The Widicus Weaver Group
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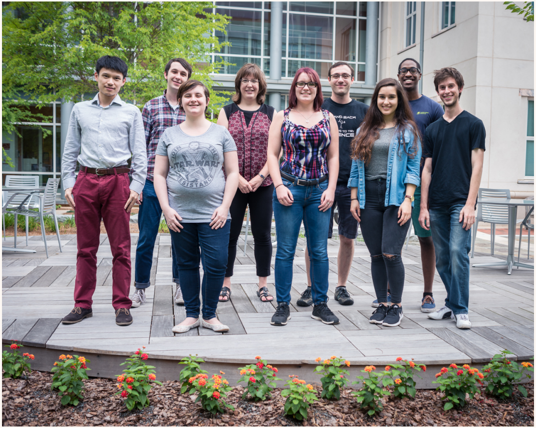
- Emory University Start-up



I expect to graduate in May 2017 and am looking for career opportunities.