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Infrared Simulations Derived from Submillimeter Wave Analyses

Douglas T. Petkie
Wright State University - Main Campus, dpetkie@yahoo.com

Rebecca A. H. Butler

Paul Helminger

Zbigniew Kisiel

Kenneth W. Jucks

See next page for additional authors

Infrared Simulations Derived from Submillimeter Wave Analyses

Douglas T. Petkie
Department of Physics, Wright State University
Rebecca A. H. Butler
Department of Physics, Pittsburg State University
Paul Helminger
Department of Physics, University of South Alabama
Zbigniew Kisiel
Institute of Physics, Polish Academy of Sciences
Kenneth W. Jucks
Earth Science Division, NASA
Brenda P. Winnewisser, Manfred Winnewisser, Frank C. De Luca
Department of Physics, Ohio State University

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The Ohio State University
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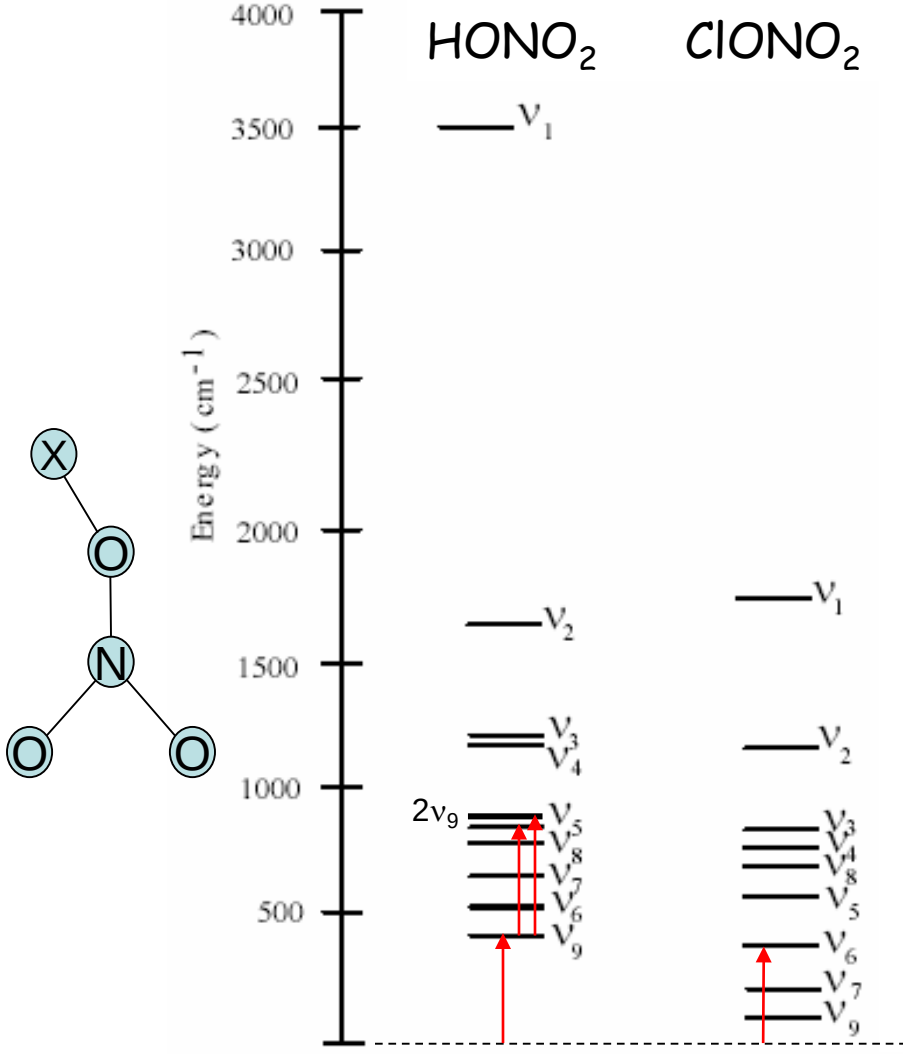
Motivation

- The synergism between mm/submm/THz and Infrared spectroscopy
  - The same physics
    - Vibrational-rotational energy levels
    - Interactions
  - Advantage of pure rotational spectra in the mm/submm/THz
    - Higher resolution
    - Resolve the thermally populated rotational spectra of heavier molecules
  - Compliment the databases (such as HITRAN, GEISA, …) used for infrared remote sensing by providing additional spectroscopic information on
    - Overlapping hot and combination bands
    - Infrared dark states

Overview

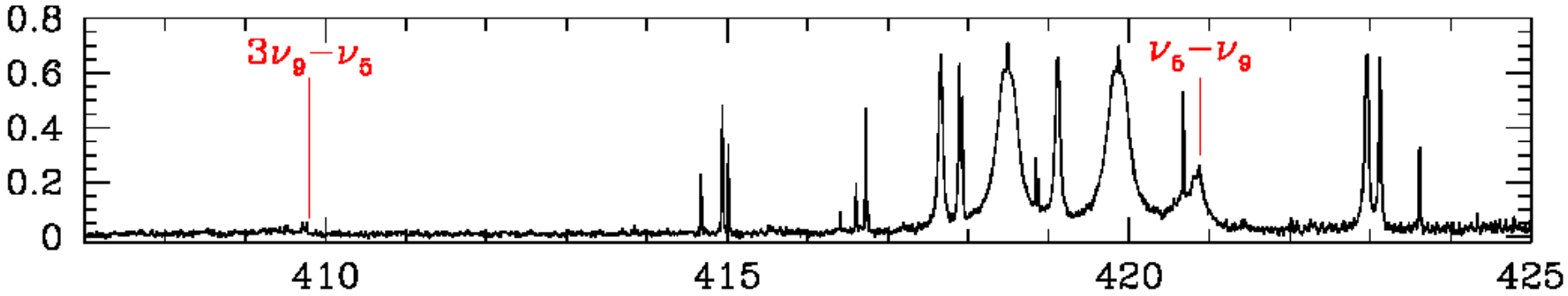
- Nitric acid, $HONO_2$
  - Simulation of the ν_5-ν_9 and $2\nu_9$-ν_9 infrared bands
- Chlorine nitrate, $ClONO_2$
  - Simulation of the ν_6-ν_0 fundamental band and the hot bands
  - Much more challenging

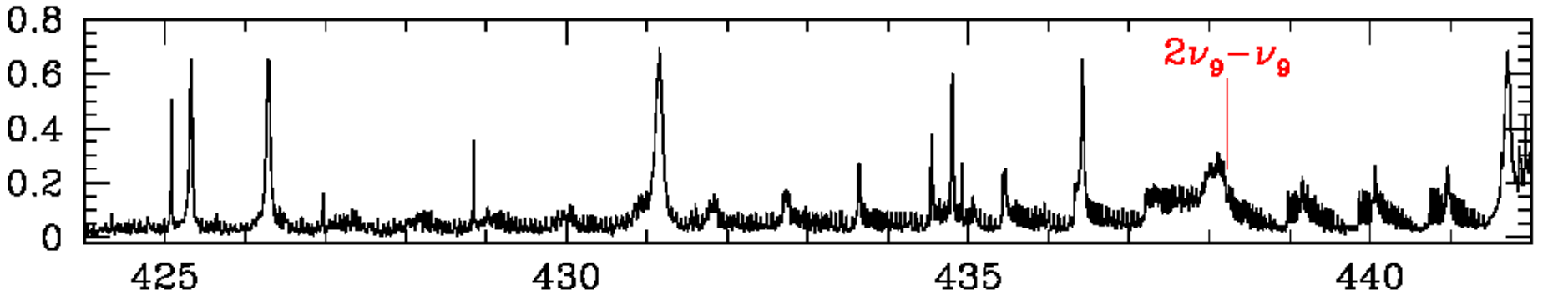


Atmospheric Spectra

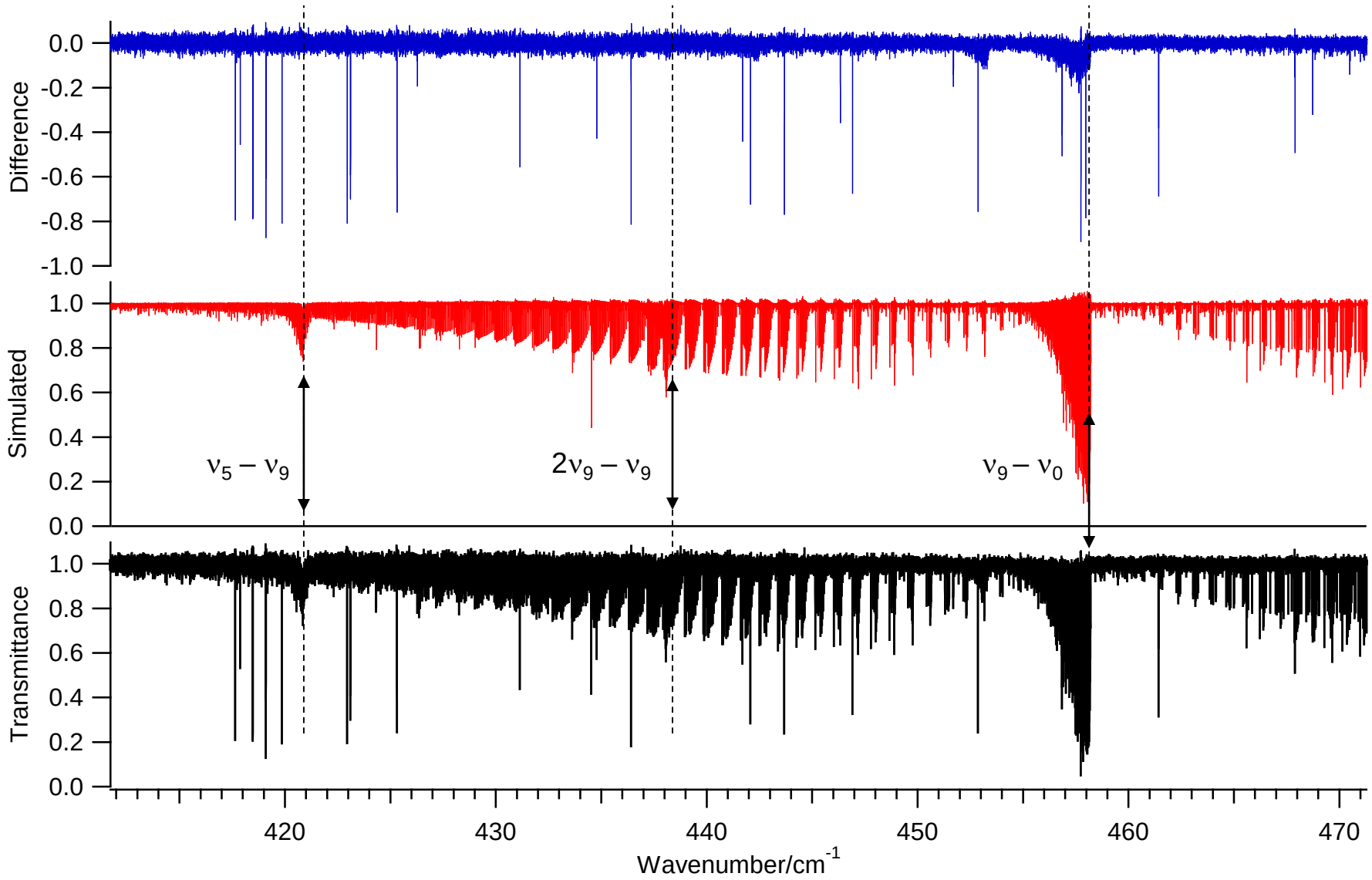
- Spectra from the balloon-borne FIRS-2 instrument

$HONO_2$



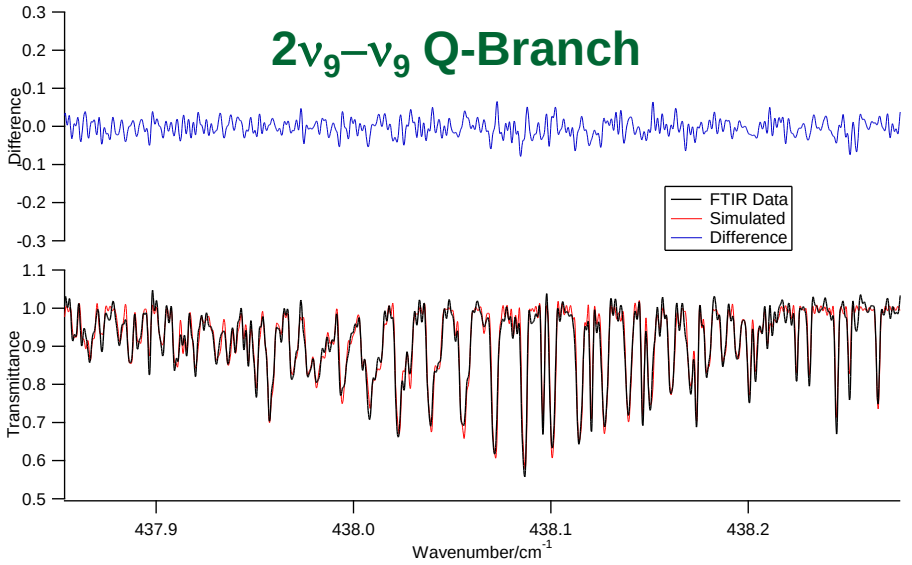


Simulation of $\nu_9-\nu_0$, $\nu_5-\nu_9$, $2\nu_9-\nu_9$ of $HONO_2$



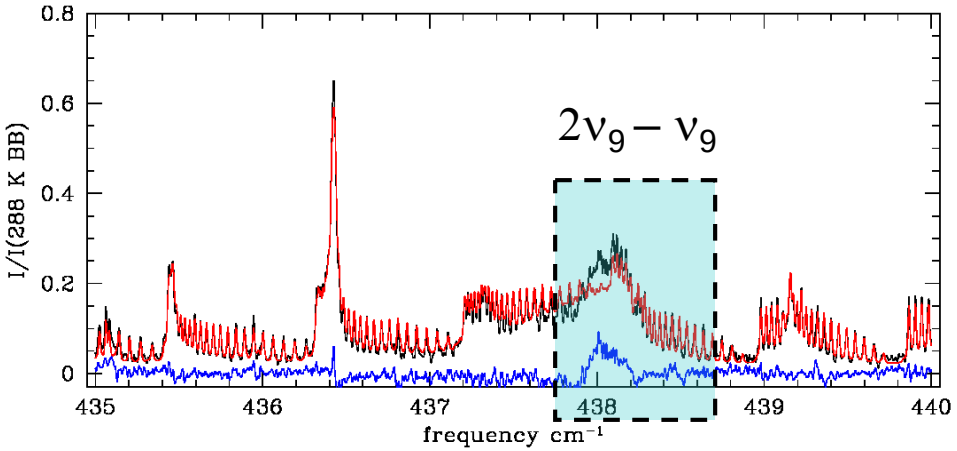
Simulation of $\nu_9-\nu_0$, $\nu_5-\nu_9$, $2\nu_9-\nu_9$ of $HONO_2$

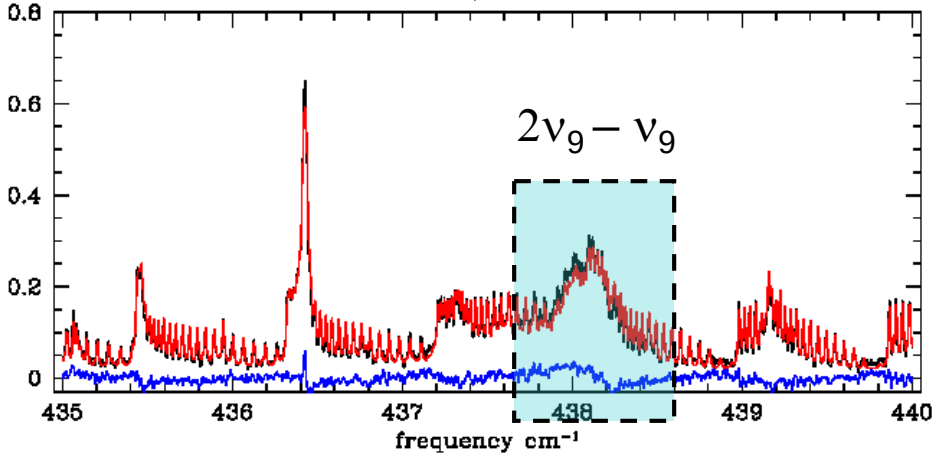
- Stringent test for infrared simulation based only on mm/submm-wave data
- Complex Spectrum
  - Fermi and Coriolis type interactions
  - Torsional splitting
- High-resolution infrared studies for comparison



Previously

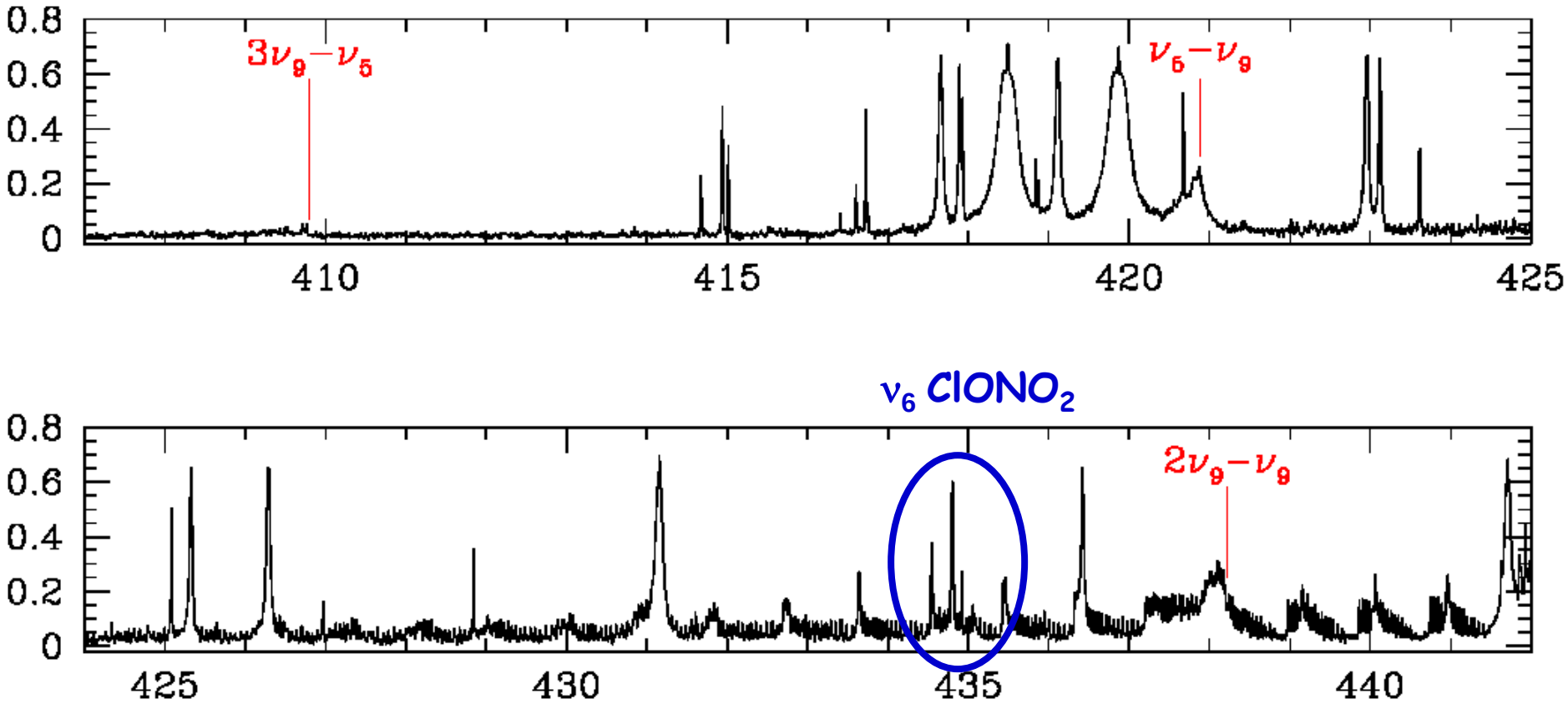
Using submm based simulation



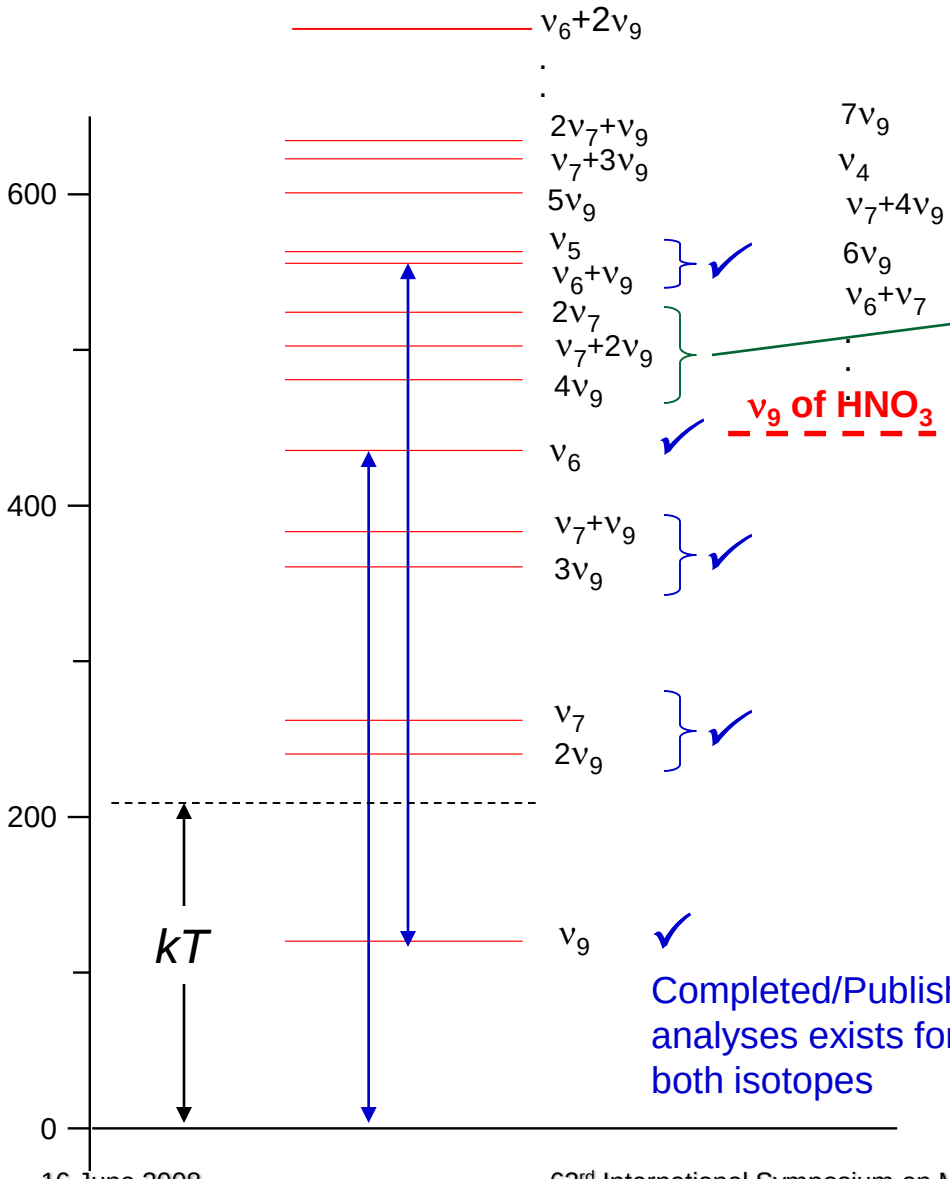


Atmospheric Spectra

- Spectra from the balloon-borne FIRS-2 instrument



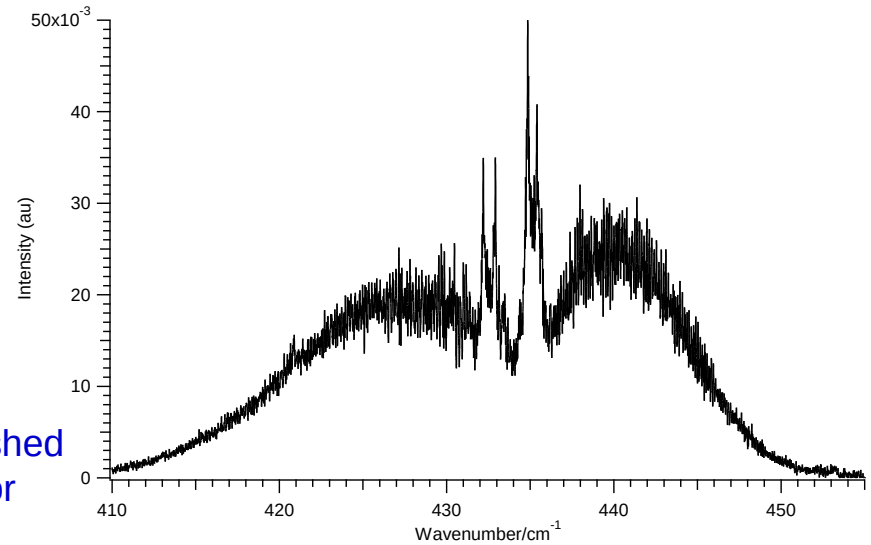
Chlorine Nitrate Analyses and Simulation



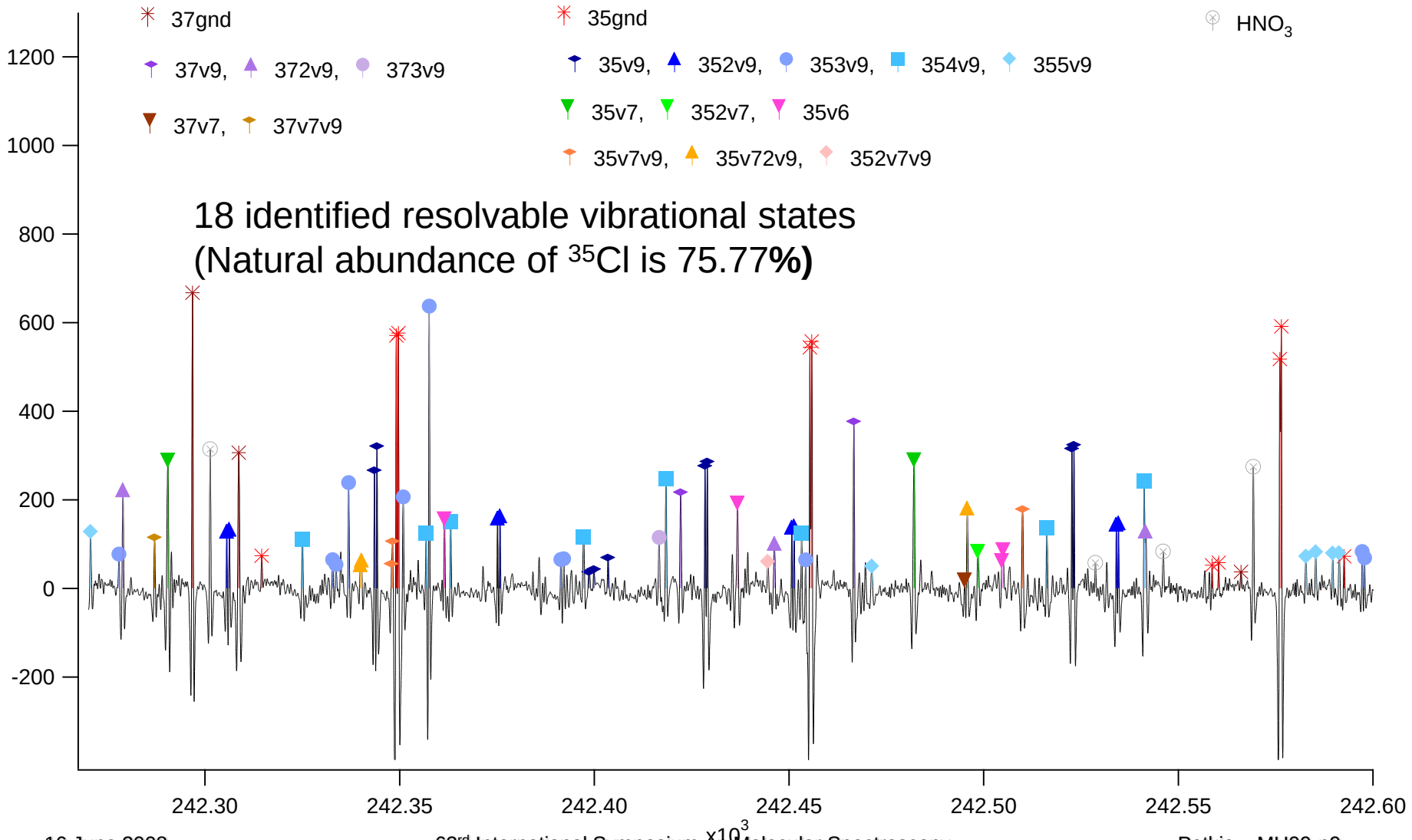
Completed/Published analyses exists for both isotopes

FC01: The Rotational Spectrum of Chlorine Nitrate ($ClONO_2$) in the Three Lowest $n\nu_9$ Polyads.

Friday @ 8:30am
1000 McPherson Lab



$ClONO_2$ scan near 242 GHz, ~350 MHz scan



ν_6-ν_0 Fundamental and Hot Bands

Laboratory spectrum of $ClONO_2$
FIRS-2 Spectrometer

Resolution ~ 0.004 cm^{-1}

Physical Considerations

- Isotope abundance

$$\frac{I_{37Cl}}{I_{35Cl}} = 0.32$$

- Dipole transition moment
  - Hybrid with both a & b type transitions
    - NO Stretch and NO_2 rock

$$\mu_a = 0.72\,D$$
$$\mu_b = 0.24\,D$$

  - Hot Bands

$$S_{\upsilon+1\leftarrow\upsilon} = \frac{8\pi^3}{3hc}\nu\frac{N}{q_\upsilon}\left[1-e^{-hc\nu/kT}\right]\left|R_{\upsilon+1\leftarrow\upsilon}\right|^2 \qquad R^2_{\upsilon+1\leftarrow\upsilon} \sim (\upsilon+1)\left(\frac{\partial\mu}{\partial Q}\right)^2$$

- Vibrational partition function

Mode, ν_i	Band Center (cm^{-1})	$q_\upsilon^i(296K)$
ν_1	1736.9	1.0002
ν_2	1292.7	1.0019
ν_3	809.4	1.0200
ν_4	778.8	1.0231
ν_8	711.2	1.0326
ν_5	561.4	1.0692
ν_6	434.0	1.1380
ν_7	273.3	1.3603
ν_9	123.7	2.2127
$q_\upsilon(296K)$		3.9545

$$q_\upsilon = \prod_{i=1}^{i=9}\left(\frac{1}{1-e^{-hc\nu_i/kT}}\right)$$

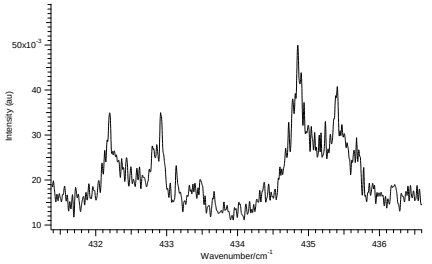
Integrated Band Intensity

$$S_{\upsilon+1\leftarrow\upsilon} = \frac{8\pi^3}{3hc}\nu\frac{N}{q_\upsilon}\left[1-e^{-hc\nu/kT}\right]\left|R_{\upsilon+1\leftarrow\upsilon}\right|^2$$

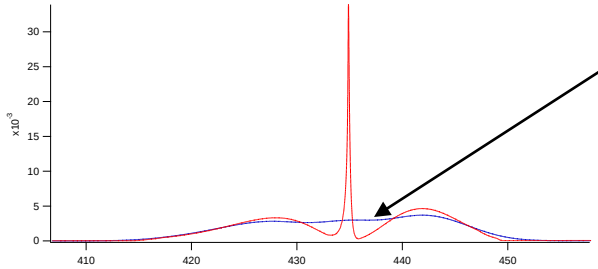
$\frac{S_{modeled}}{S_{Total}} \approx 0.35$ Fundamental and first hot band for each isotope

Simulation ν_6-ν_0 Fundamental and Hot Bands

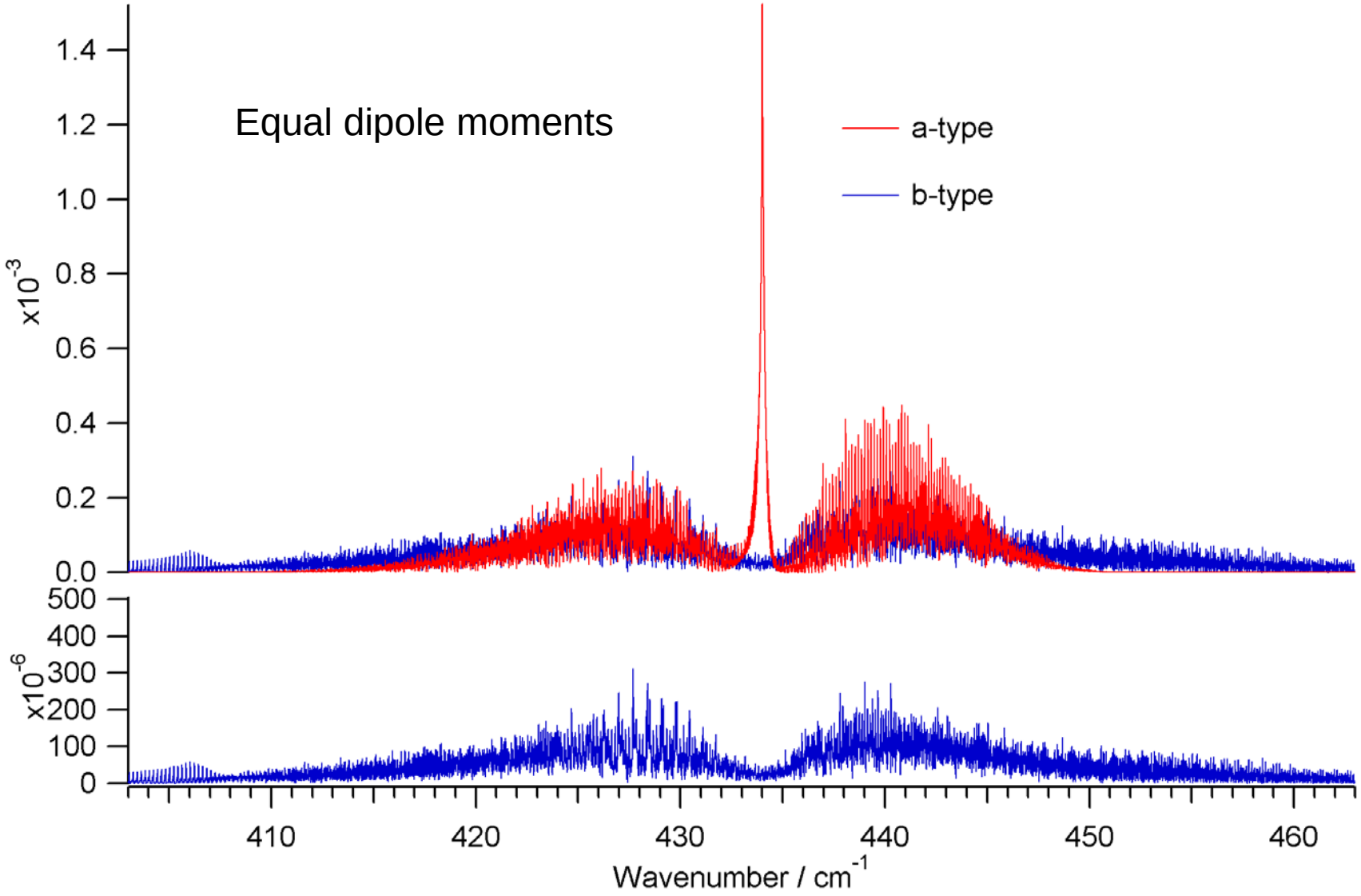
- Method
  - Simulated the fundamental and first hot band
  - Fit for the band centers (fundamental + ν_9 hot band)
    - Dominated by Q-branch position
    - Isotopes included
  - Fit a/b-type moments
  - Use a smoothed spectrum to account for left out hot bands
    - Q-branch intensity was also smoothed out
    - Use same a/b-type moment ratio



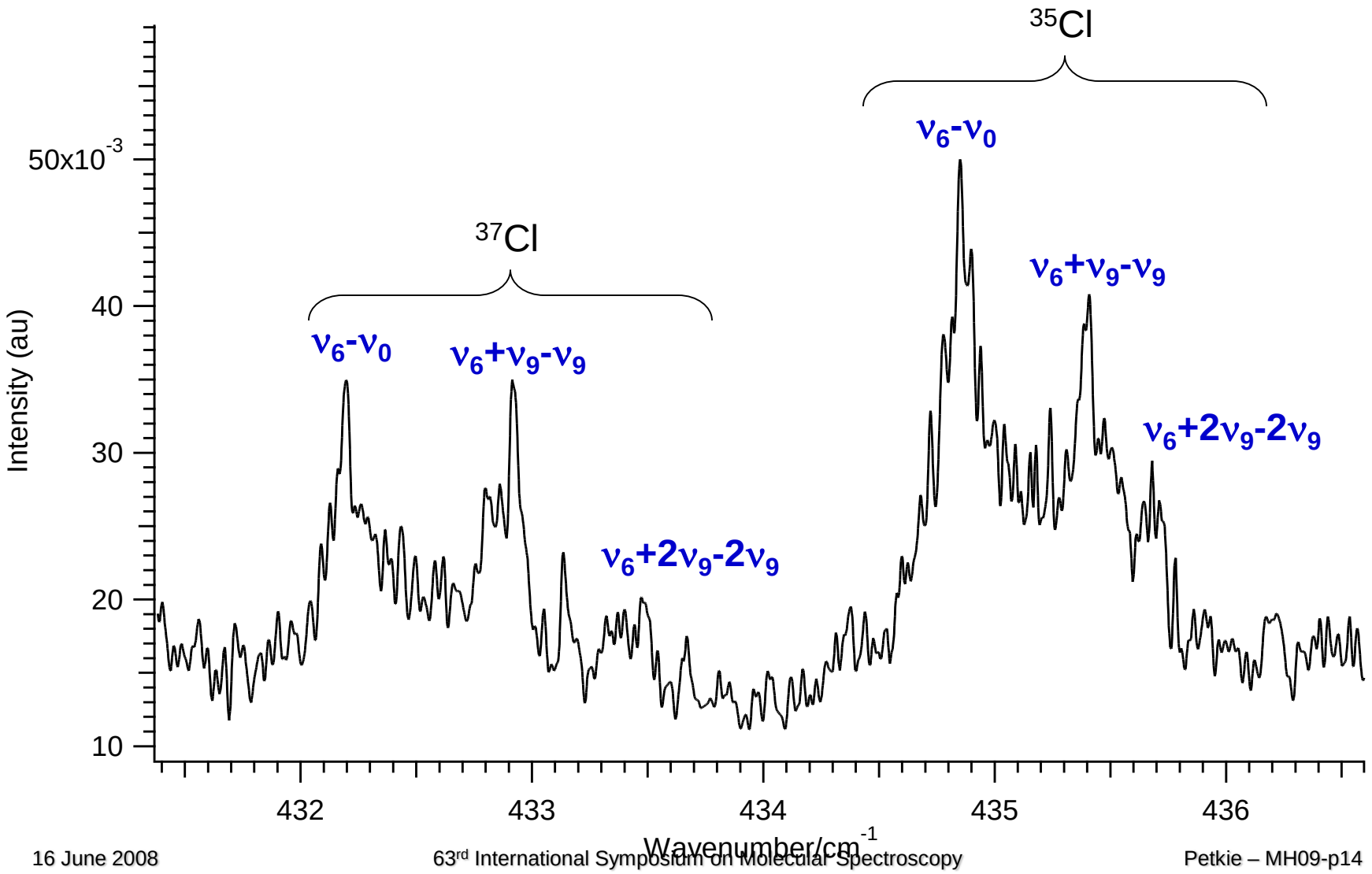
$$\frac{S_{\text{mod eled}}}{S_{Total}} \approx 0.35$$



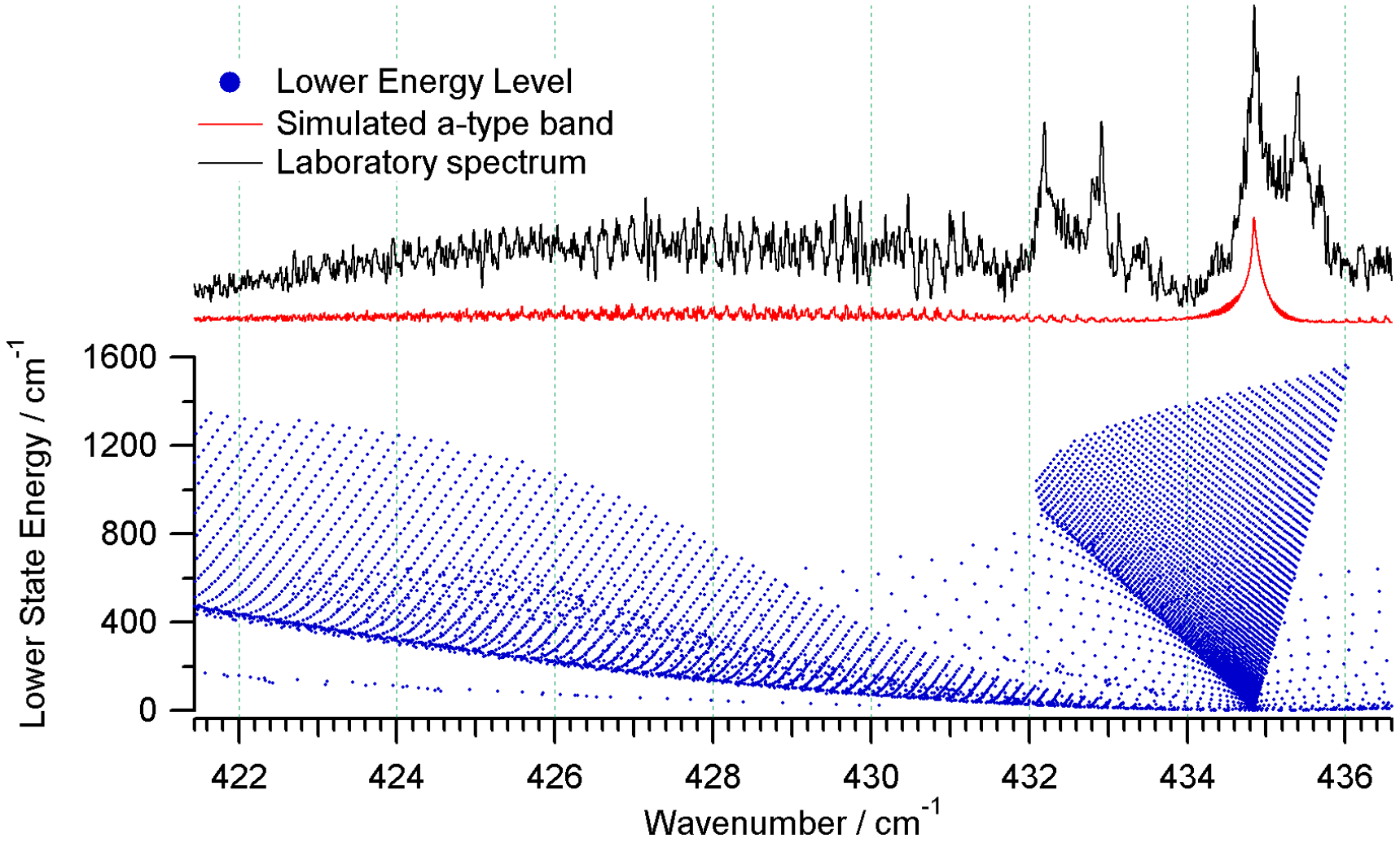
A-type vs B-type



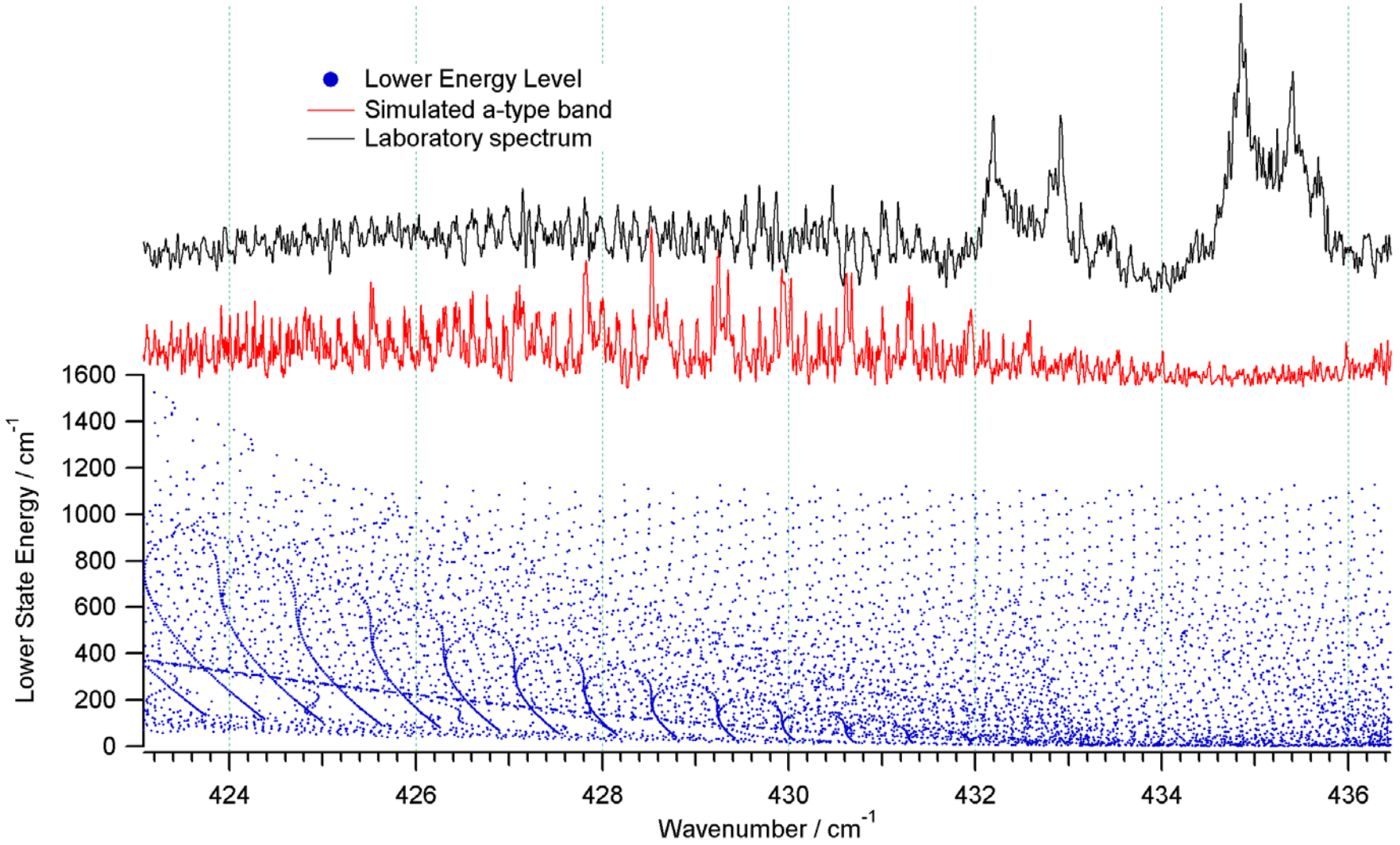
ν_6-ν_0 Fundamental and Hot Bands



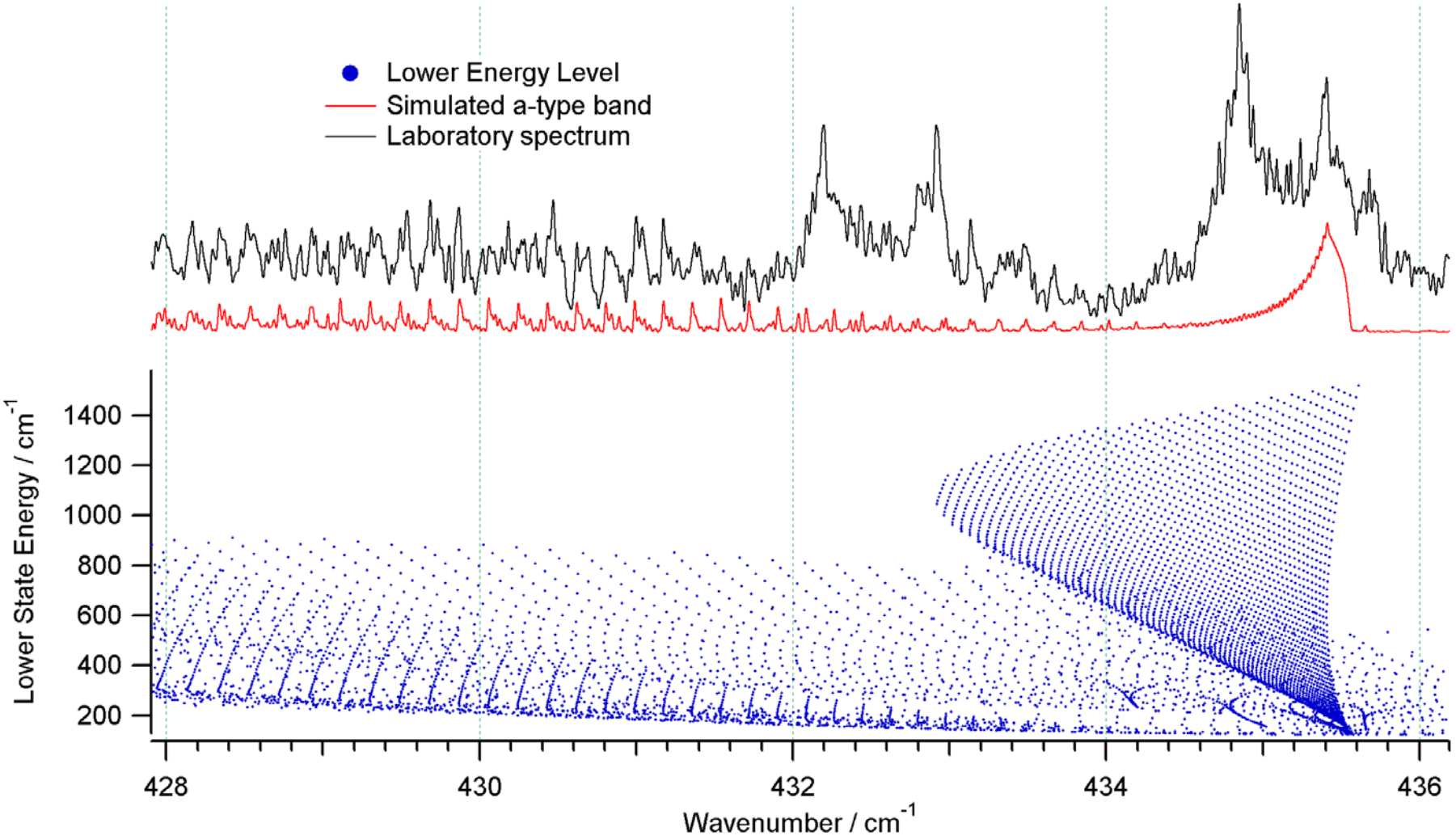
ν_6-ν_0 a-type Simulation



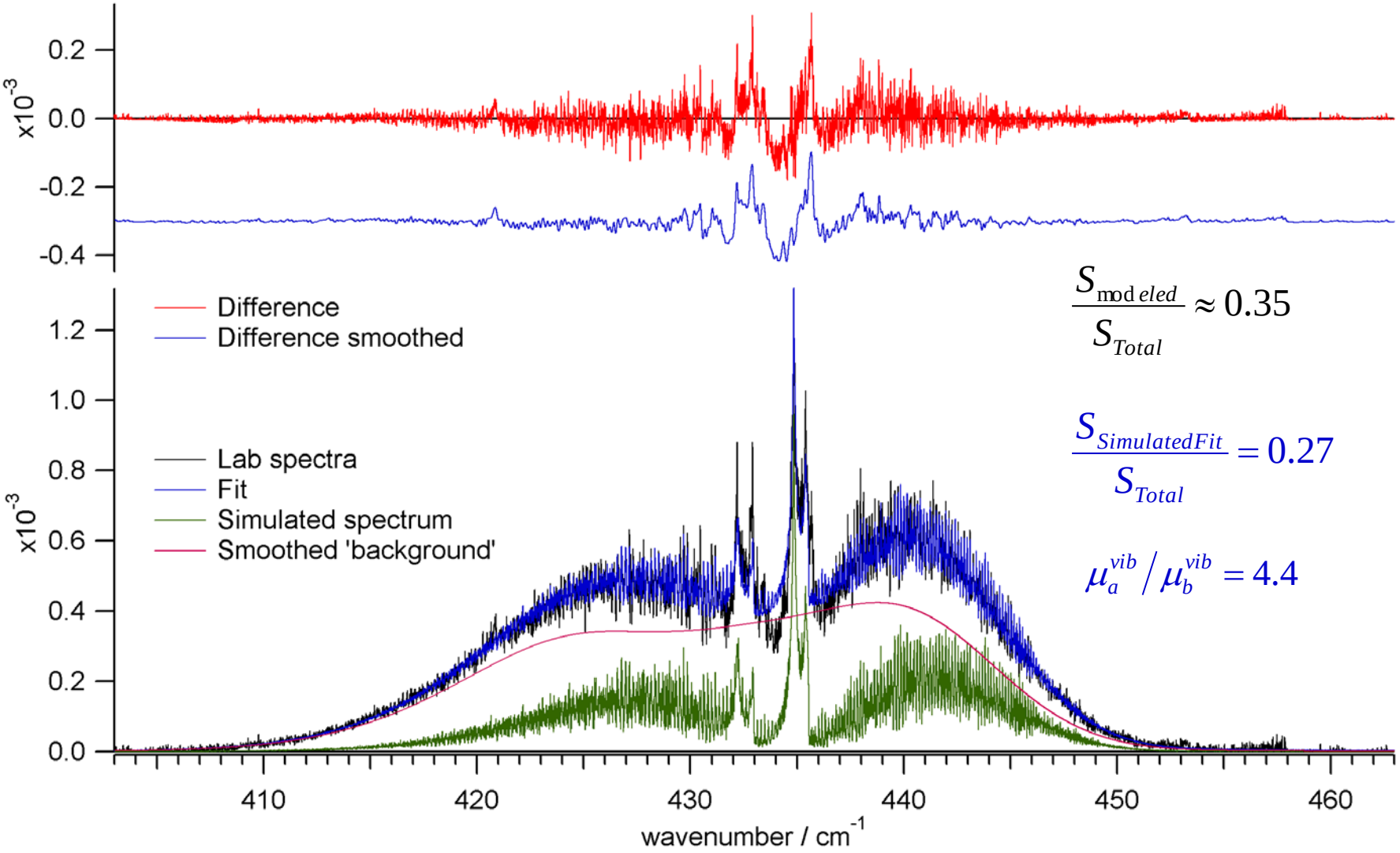
ν_6-ν_0 b-type Simulation



$\nu_6\nu_9$-ν_9 a-type Simulation



Overall Simulation

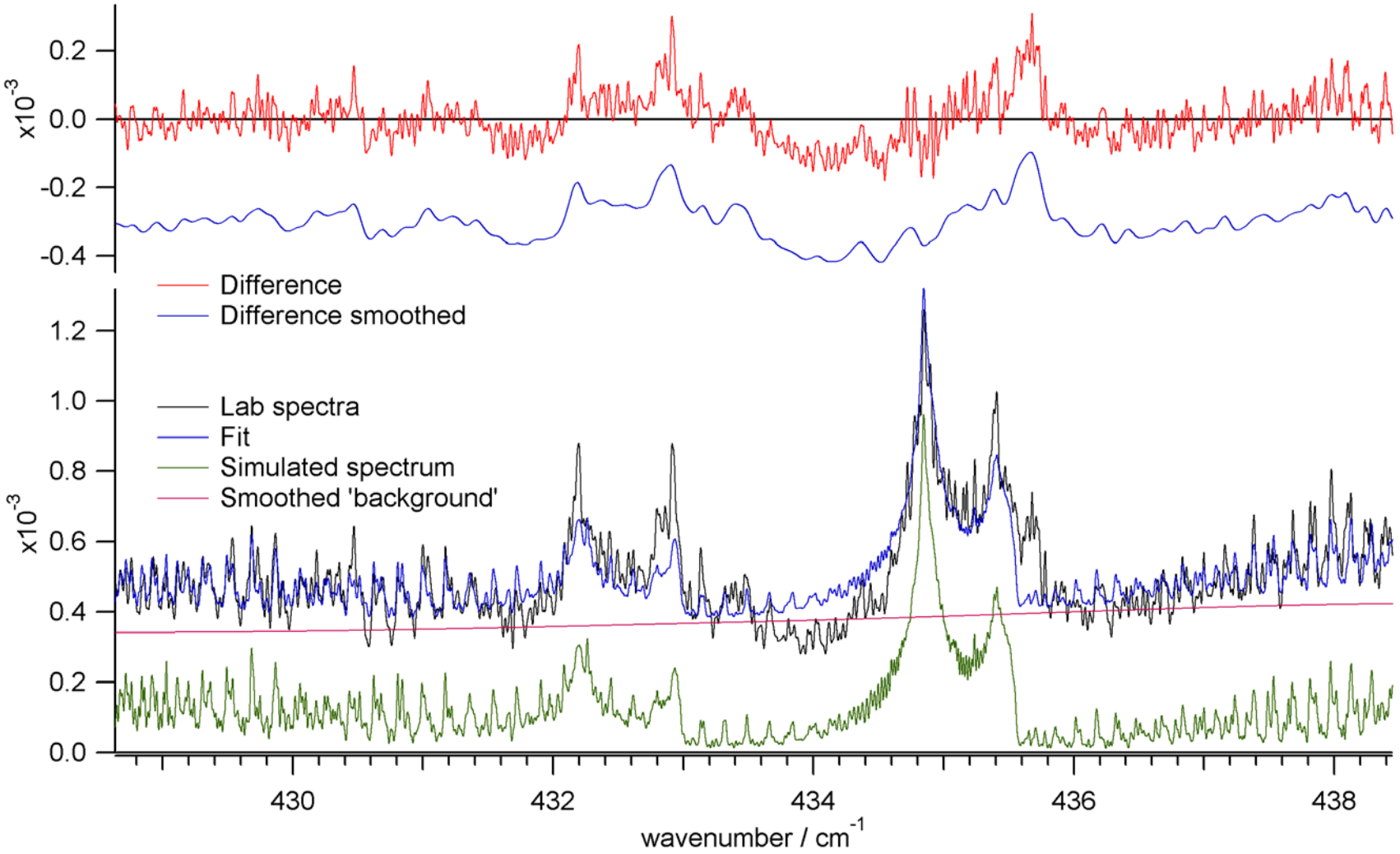


$$\frac{S_{\mathrm{mod}\,eled}}{S_{Total}} \approx 0.35$$

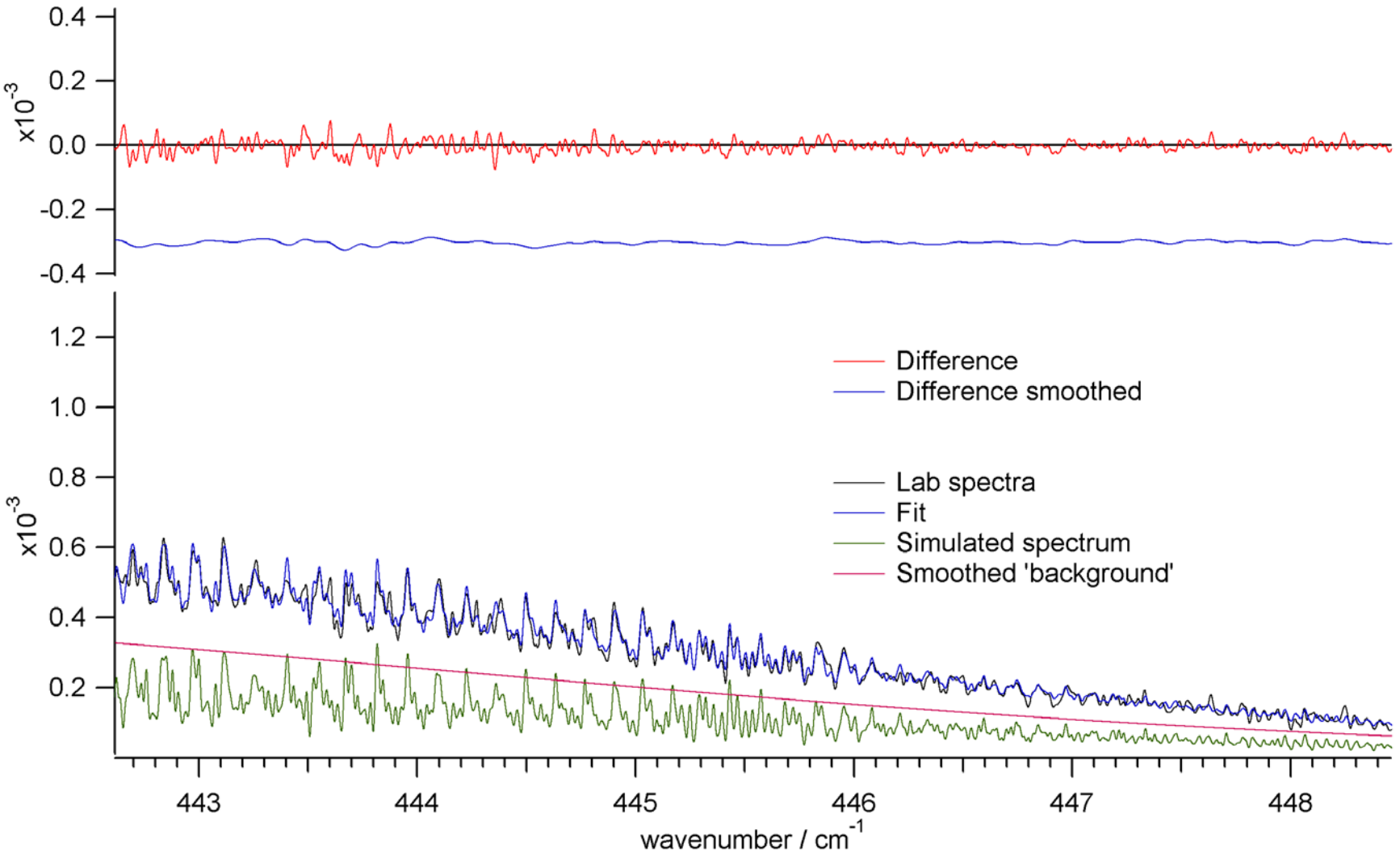
$$\frac{S_{SimulatedFit}}{S_{Total}} = 0.27$$

$$\mu_a^{vib} \,/\, \mu_b^{vib} = 4.4$$

Q-Branch Region



R-Branch Region

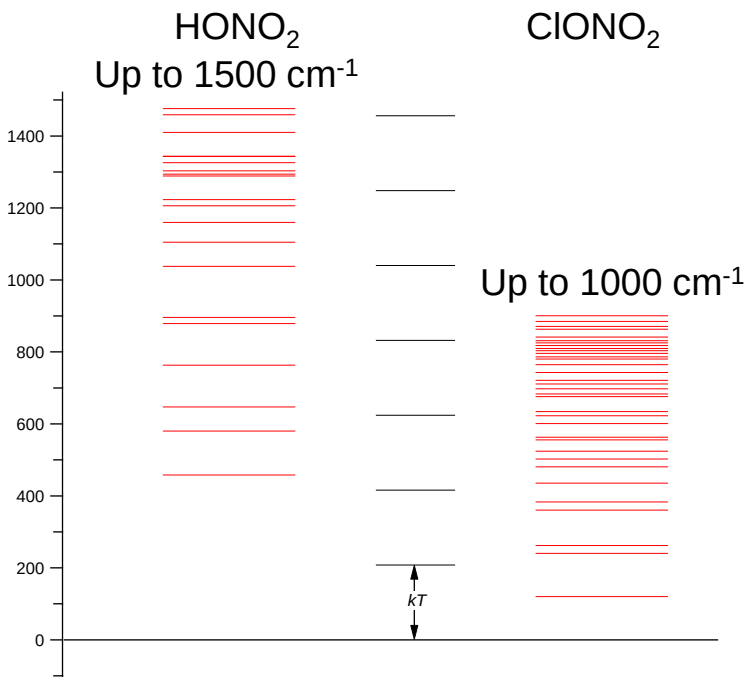


Conclusions and Future Work

- Successfully simulated the fundamental and first hot band
  - Significant features Q/P/R branch regions
  - Included the analysis of a dyad, $\nu_5/\nu_6\nu_9$

- Total integrated intensity and dipole transition moments are very reasonable

- Incorporate
  - nitric acid
  - Incorporate next set of hot bands



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