

## Determination of vibrational state energy from THz rotational spectra: Urea assignment of the ground and first eight excited vibrational states

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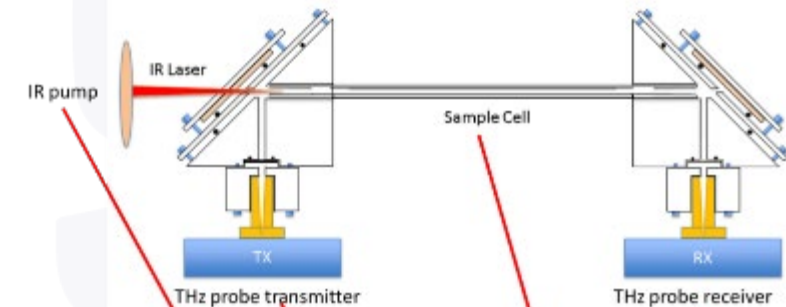
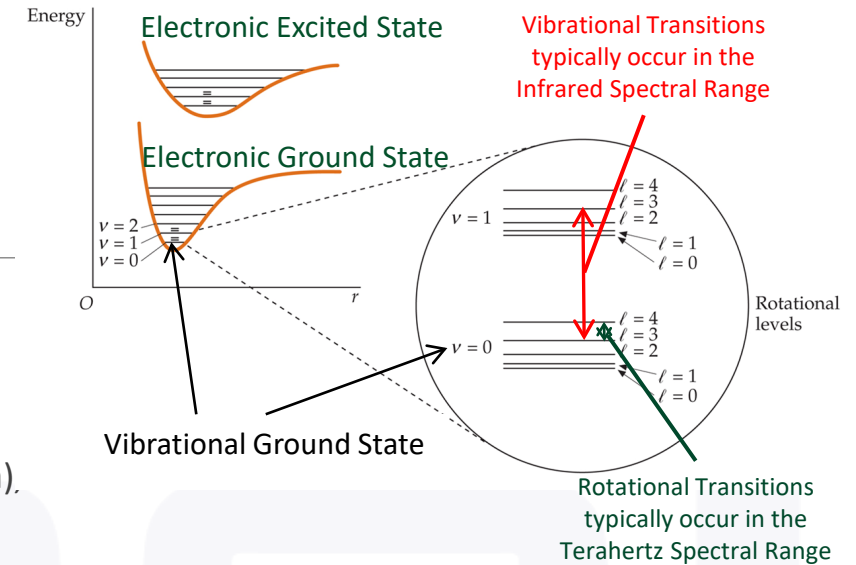
AFRL Sponsor: Dr. Steve Kim

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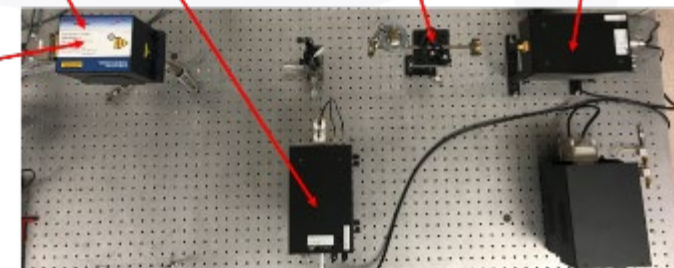
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# Motivation

- This research is motivated by development of multispectral molecular sensors with specific focus on terahertz (THz, rotational spectra) and infrared (IR, vibrational spectra).
  - Such sensors can be used for detecting a wide range of chemicals with applications in human performance, propulsion, chemical biodefense, and other general sensing applications.
- Rotational spectra provide very sensitive and selective chemical detection for lighter (<100 Da), polar, volatile species.
  - In larger molecules, due to a large number of vibrational modes, exhibit spectral congestion and high detection limits.
  - An IR-THz multispectral sensor can overcome some of these limitations for detection of larger species.
- The purpose of this study is to establish a scheme to identify rotational transitions in linked ground and excited vibrational states to facilitate multispectral detection.
  - This connection can be utilized to pump signal from a congested line using an IR source to an excited vibrational state to then be probed by THz with greater signal than the other nearby lines.
  - This may improve the detection of weakly absorbing molecules or heavily cluttered spectra.
- To determine suitable states for connection, the precise energies of the rotational state and the vibrational state are required.
  - Rotational energies can be predicted from a quantum mechanical Hamiltonian with molecule specific parameters.
  - Vibrational energies may not be as easily treated by a Hamiltonian and instead be determined empirically.



Daylight Solutions  
QCL laser  
60 mW,  
963 -1028  $\text{cm}^{-1}$

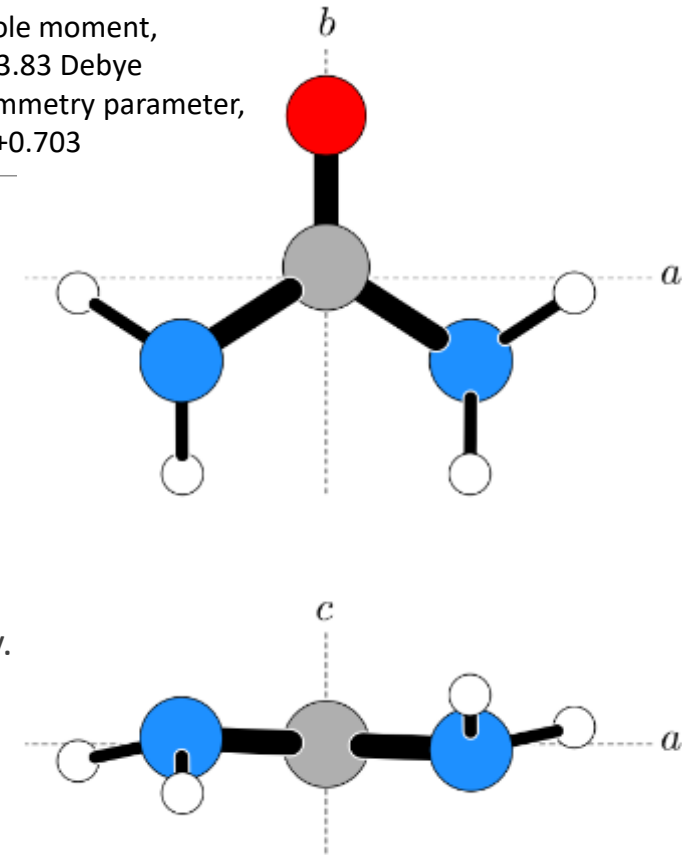


Multispectral IR-THz experiment configuration

# Background

- The strength of a spectral feature is proportional to the fraction of a sample in the lower state of the spectral transition [1].
- Molecules are distributed across their energy states described by a Boltzmann distribution.
  - Spectral transitions will have intensity scaled by  $e^{\frac{-E_l}{kT}}$  [1].
    - $E_l$  is the energy of the lower state,  $k$  is the Boltzmann factor, and  $T$  is the gas temperature.
- We can use this intensity factor along with other known experimental parameters to infer the lower state energy of a spectral transition.
  - Higher energy vibrational states will have lower intensity compared to those with lower energy.
  - Comparing two spectral features can enable the calculation of the difference in vibrational energy between the states.
- We chose, as a demonstration, urea which has several excited states visible, near room temperature, alongside its ground state spectra.
  - Urea is an important nitrogen bearing industrial and biological molecule and had not been previously analyzed to high microwave/THz frequencies.
    - Prior rotational spectroscopy of urea in its ground vibrational state was commenced by Brown [2] between 5 and 50 GHz.
    - Later extended using Fourier transform microwave spectroscopy in a wave guide by Kasten [3] and in supersonic, laser ablated sample into a cavity by Kretschmer [4].

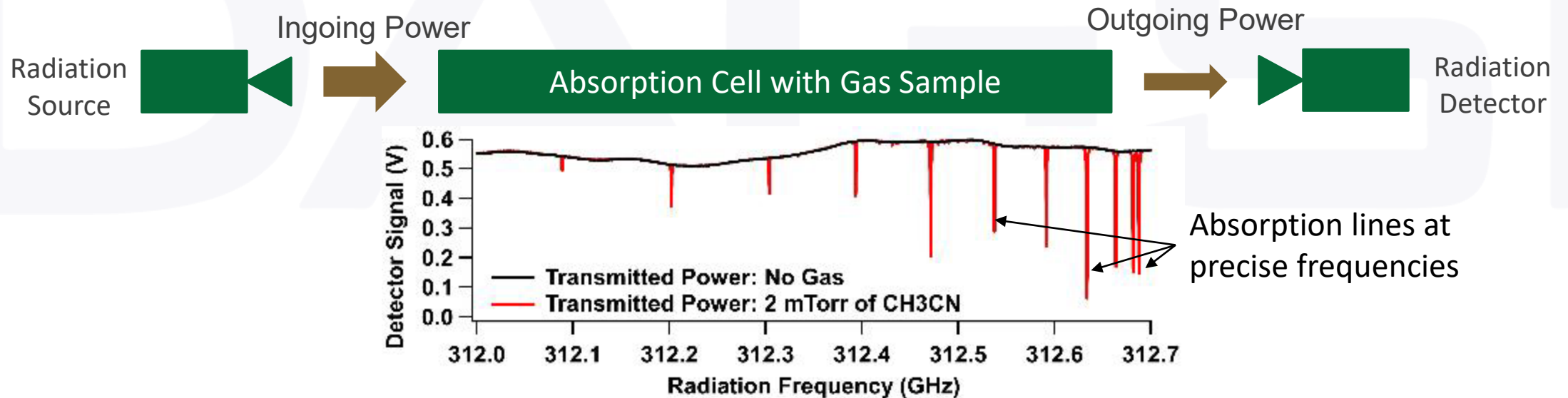
Dipole moment,  
 $\mu = 3.83$  Debye  
Asymmetry parameter,  
 $\kappa = +0.703$



Equilibrium urea structure and its principal axes.  
The electric dipole is oriented along the b axis

# Terahertz (THz) Rotational Spectroscopy

- Rotational absorption spectroscopy is an optical method to detect and measure a gaseous compound by probing the quantized rotational energies dependent on molecular structure.
  - Rotational absorption features are narrow regions of radiation frequency where the gas absorbs the incident radiation reducing the power measured at a detector. These narrow features are commonly referred to as absorption lines.
  - The intensities and widths of absorption lines describe the amount of gas present in a sample.
  - Molecules have rotational absorption lines at frequencies in the range a few GHz ( $10^9$  Hz) to several THz ( $10^{12}$  Hz). [1]

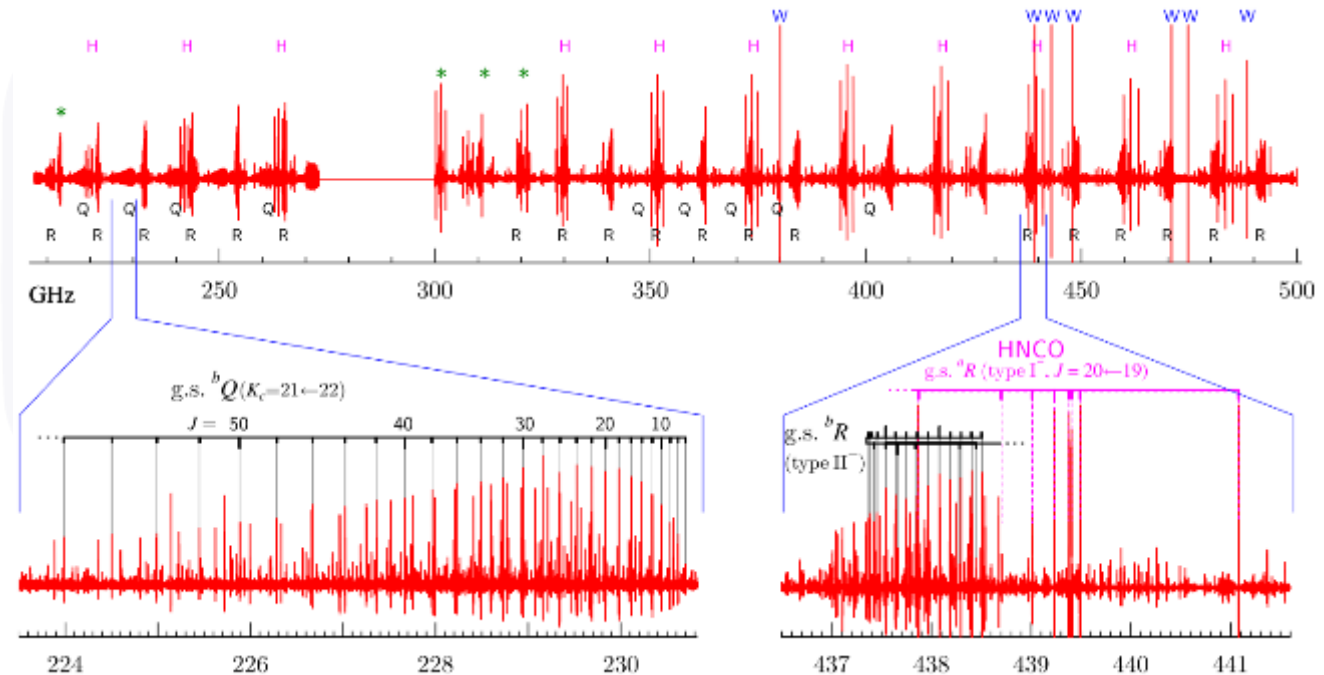


# Spectral Acquisition

- Urea spectra were acquired over a range of 210-270 GHz and 350-500 GHz using sources and heterodyne detectors from Virginia Diodes (VDI) [5].
- A pure sample of urea, heated to increase its vapor pressure, was introduced to a 90 C cell as a continuous flow maintain at consistent pressure.
  - Pressure was maintained around 2 mTorr for the lower frequency range and around 4 mTorr for the upper frequency range.
  - Due to heating, some of the urea was decomposed into isocyanic acid which was visible in the urea spectrum.
  - Isocyanic acid line frequencies were used to confirm the accuracy of measured frequencies at the detector.



Laboratory spectrometer as WSU

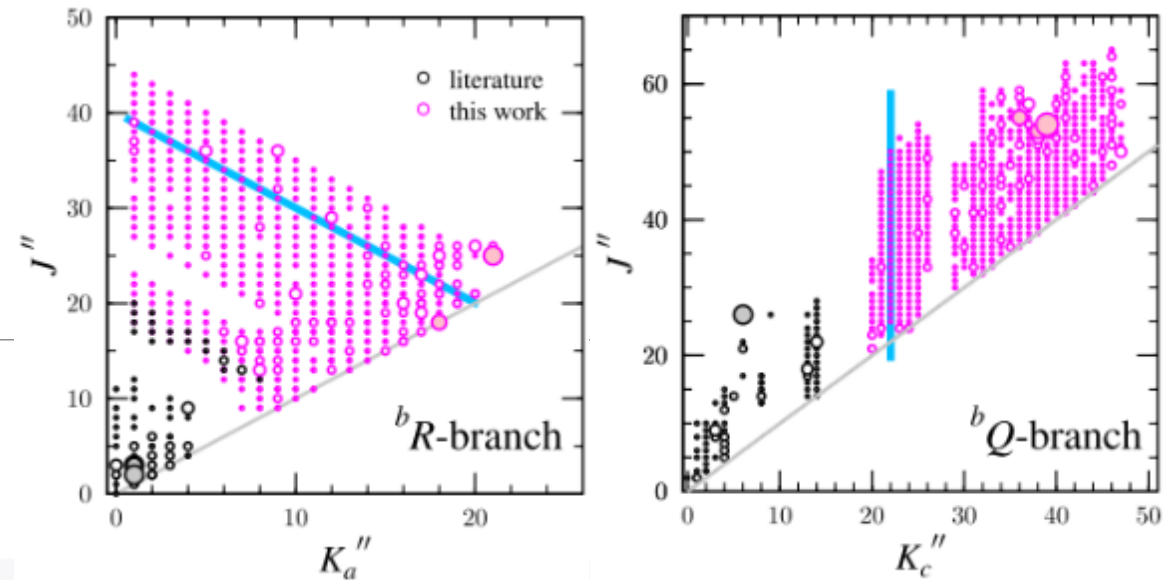


Measured spectra of urea from 210 – 500 GHz. Many Q and R branches were visible from the ground and excited vibrational states. Also present are lines from isocyanic acid (HNCO), a product of urea degradation at higher temperatures, and water from ingress of ambient air into the spectroscopic cell.

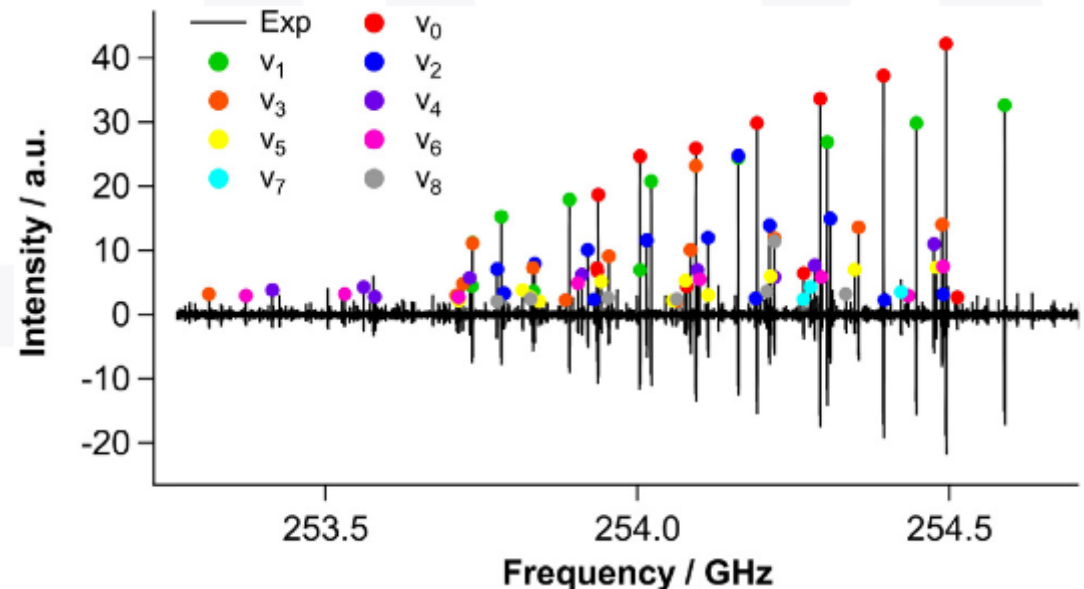


# Urea Assignment

- In order to calculate the vibrational energy of excited states, intensities of each spectral transition were calculated.
  - The intensities were determined by assigning each line in the spectrum to a quantum state and fitting constants of a rotational Hamiltonian to the assignments using SPFIT, software maintained by NASA's JPL for this purpose [6].
- Vibrational states were fitted individually except in cases where states interacted which required a coupled, simultaneous fit.
- For the excited states,
  - The lowest excited state was unperturbed and was assigned using a single state fit.
  - The 2<sup>nd</sup> and 3<sup>rd</sup> were found to be coupled and were fitted together with treatment for Coriolis coupling.
  - The 4<sup>th</sup> and 5<sup>th</sup> state were also fitted with Coriolis coupling
  - The remaining excited states were generally too weak to observe perturbations and were therefore fitted with single state models.



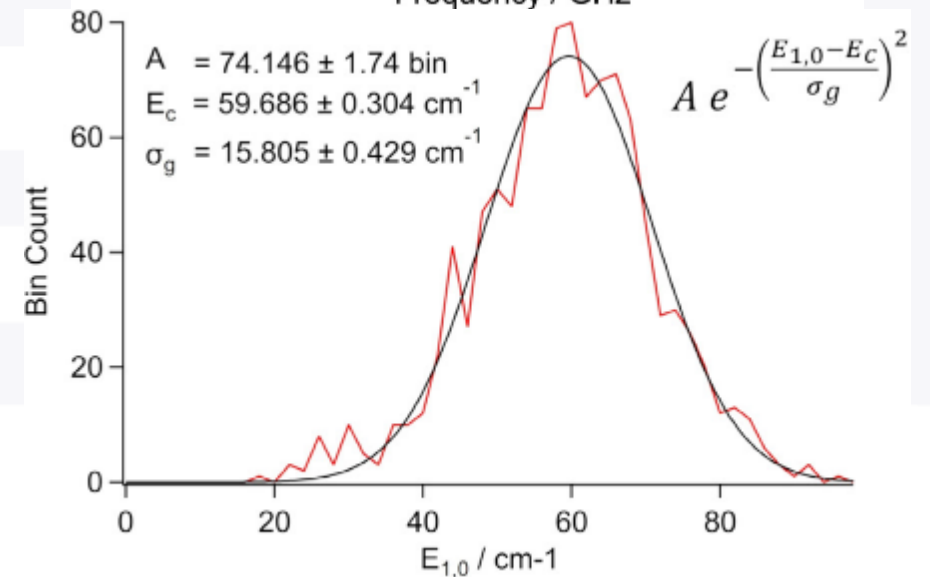
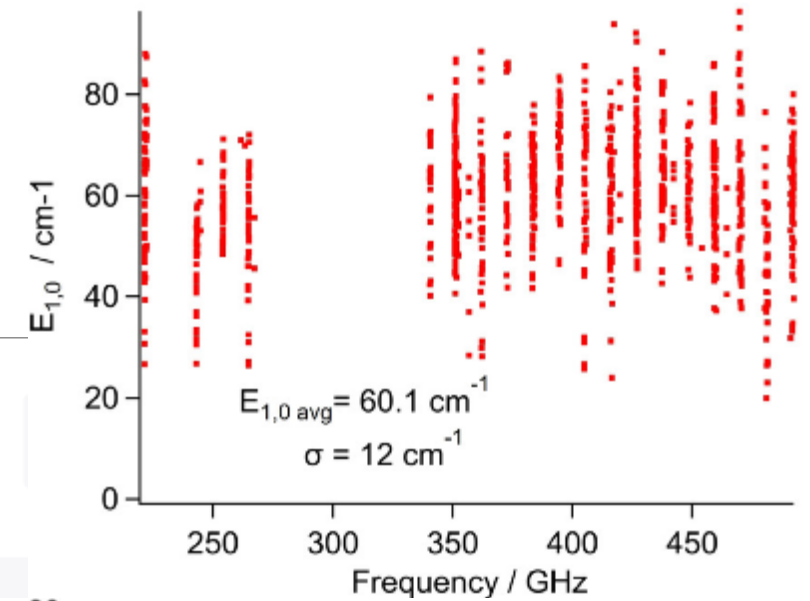
Assignments of the ground state R and Q branches from literature and those added by this work



A narrow frequency region of R branch spectra of urea and its eight lowest vibrationally excited states

# Vibrational Energy Determination

- Assigned lines enabled the calculate of intensities using spectral prediction software SPCAT [6] a sister program to SPFIT.
- The experimental intensities,  $\alpha_{peak}$ , were related to those determined from SPCAT by
  - $$\alpha_{peak} = \frac{\alpha_{SPCAT}}{\delta\nu_D} n \frac{e^{-\frac{E_{vib}}{kT}}}{Q_{vib}}$$
    - $\alpha_{SPCAT}$  is the calculated intensity,  $\delta\nu_D$  is the doppler line width,  $n$  is the number density of the gas,  $E_{vib}$  is the vibrational energy,  $k$  is the Boltzmann constant,  $T$  is gas temperature, and  $Q_{vib}$  is the portion of the partition function coming from the vibrational states.
- Energies of the vibrational states were determined by ratio of the power normalized experimental R branch line intensities.
  - The vibrational energy difference between two lines was determined by
    - $$\Delta E_{v'',v'} = kT \ln \left( \frac{\alpha'_{peak} \alpha''_{SPCAT} v'}{\alpha''_{peak} \alpha'_{SPCAT} v''} \right)$$
  - To minimize error, energies were only calculated from pairs of lines within 2 GHz of one another.
  - Energies were calculated by pairing each line with all other lines in each other vibrational state within range.
  - These pairs and average energies are presented in the following slide along with associate standard deviations.



Calculated vibrational energy difference between the lowest excited state and the ground state for each line pair. Histogram of the energies shows that they are normally distributed.

# Line Pairs and Relative Vibrational Energy

	$\nu_0$	$\nu_1$	$\nu_2$	$\nu_3$	$\nu_4$	$\nu_5$	$\nu_6$	$\nu_7$	$\nu_8$
$N^a$	179	182	150	128	100	121	106	30	53
The number of matched line pairs for calculation of energy of state $\nu''$ relative to state $\nu'$									
$\nu_1$	1063								
$\nu_2$	976	860							
$\nu_3$	851	763	743						
$\nu_4$	556	506	497	447					
$\nu_5$	833	683	655	574	400				
$\nu_6$	585	536	516	486	392	432			
$\nu_7$	241	216	192	160	91	161	109		
$\nu_8$	425	333	338	281	206	295	215	81	
Relative energy and uncertainty ( $\text{cm}^{-1}$ ) of state $\nu''$ relative to state $\nu'$									
$\nu_1$	$60.1 \pm 12.1$								
$\nu_2$	$253.6 \pm 17.3$	$192.4 \pm 17.1$							
$\nu_3$	$266.6 \pm 17.5$	$206.8 \pm 17.6$	$13.6 \pm 21.3$						
$\nu_4$	$398.6 \pm 20.5$	$337.4 \pm 20.9$	$146.0 \pm 23.5$	$130.8 \pm 24.3$					
$\nu_5$	$419.4 \pm 24.8$	$359.3 \pm 24.6$	$166.1 \pm 28.6$	$151.7 \pm 28.1$	$21.1 \pm 27.7$				
$\nu_6$	$453.5 \pm 26.0$	$393.3 \pm 25.9$	$199.1 \pm 27.9$	$186.1 \pm 29.0$	$54.1 \pm 30.8$	$32.6 \pm 32.5$			
$\nu_7$	$506.5 \pm 21.5$	$444.2 \pm 24.7$	$247.5 \pm 28.6$	$238.1 \pm 28.2$	$111.3 \pm 26.0$	$83.7 \pm 30.5$	$54.2 \pm 33.8$		
$\nu_8$	$570.5 \pm 28.6$	$508.4 \pm 30.4$	$315.3 \pm 32.9$	$303.3 \pm 34.0$	$177.3 \pm 34.6$	$152.2 \pm 35.8$	$122.1 \pm 37.0$	$67.0 \pm 29.0$	

<sup>a</sup> N is number of selected lines in each vibrational state. Due to the frequency gating not all lines were paired between vibrational states. The relative energy between state was determined by averaging all energies for each state pair.



# Vibrational Energy Determination

- Ratios between the ground and excited states returned reasonable energies with moderate errors.
- An attempt was made to further reduce errors by incorporating remaining combination differences into linear system 36 of equations.
  - $E_{v_1} = \Delta E_{v_1, v_0}$ ,  $E_{v_2} - E_{v_1} = \Delta E_{v_2, v_1}$ , etc
  - Due to uncertainty in each energy measurement, there is no explicit solution to the system, but can use linear regression to minimize error across all combinations.
  - The result of the linear regression is presented on the right and shows tighter errors in reasonable agreement with other measurements.

	$E_{\text{vib}}/\text{cm}^{-1}$	S <sup>a</sup>	$\nu_{\text{lit}}/\text{cm}^{-1}$
$v_0$	0	s	
$v_1$	$61 \pm 8$	s	58 <sup>b</sup>
$v_2$	$254 \pm 10$	a	227 <sup>c</sup> , 228 <sup>d</sup> , $\approx 240^b$
$v_3$	$267 \pm 10$	s	232 <sup>c</sup> , 233 <sup>d</sup>
$v_4$	$398 \pm 10$	s	$\approx 380^b$ , 408 <sup>d</sup> , 409.1 <sup>e</sup>
$v_5$	$420 \pm 12$	a	442 <sup>d</sup> , 444.8 <sup>e</sup> , 445.1 <sup>f</sup>
$v_6$	$453 \pm 12$	s	479 <sup>d</sup> , 479.9 <sup>e</sup> , 483.7 <sup>f</sup> , 485 <sup>c</sup>
$v_7$	$505 \pm 11$	–	500 <sup>d</sup> , 500.5 <sup>f</sup> , 501.0 <sup>e</sup>
$v_8$	$571 \pm 13$	–	549 <sup>b</sup> , 552 <sup>c</sup> , 558 <sup>b</sup> , 571 <sup>g</sup> , 578 <sup>c</sup> , 580 <sup>d</sup> , 582.4 <sup>f</sup> , 582.9 <sup>e</sup>

<sup>a</sup> Symmetry on rotation around the C<sub>2</sub> axis determined from nuclear spin statistical weights. <sup>b</sup> Ref. [7], solid pellet at room temperature, 58 and 380 cm<sup>-1</sup> Raman, otherwise ir. <sup>c</sup> Ref. [8], inert gas matrix isolation at 20 K, deposited from 120 °C. <sup>d</sup> Ref. [9], inert gas matrix isolation at 10 K, deposited by slow sublimation from 35 °C. <sup>e</sup> Ref. [10], inert gas matrix isolation at 8 K, deposited from 77 °C. <sup>f</sup> Ref. [11], inert gas matrix isolation at 19 K, deposited from 100–180 °C. <sup>g</sup> Ref. [12], gas phase at 120 °C.

# Conclusions

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- Urea spectra has been assigned enabling the accurate detection and quantification of gas phase urea with THz spectroscopy.
  - This data analysis is useful for terrestrial sensing and for astronomical observations.
  - This assignment was published in the Journal of Molecular Spectroscopy
    - D. J. Tyree, T. W. Chapman, I. R. Medvedev, and Z. Kisiel, "Rotational spectroscopy of urea up to 500 GHz: The ground and eight excited vibrational states," J. Mol. Spectrosc., vol. 390, p. 111706, Nov. 2022, doi: 10.1016/J.JMS.2022.111706.
- Careful treatment of intensities from over 5000 lines of urea enabled estimation of vibrational energies of excited states from a single spectral acquisition.
  - The energies determined were calculated with narrow ranges of error.
  - The energies show reasonable agreement with literature.
  - The method is easily transferred to other compounds.
- We have already begun this treatment of isoprene which is a biological molecule of interest and a good candidate for multispectral sensing.

# Acknowledgements and References

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