Continuous-Wave Cavity Ringdown Study of the $^{14}N_2^+$ Meinel System 2-1 Band and the First Positive Band System of N_2^*

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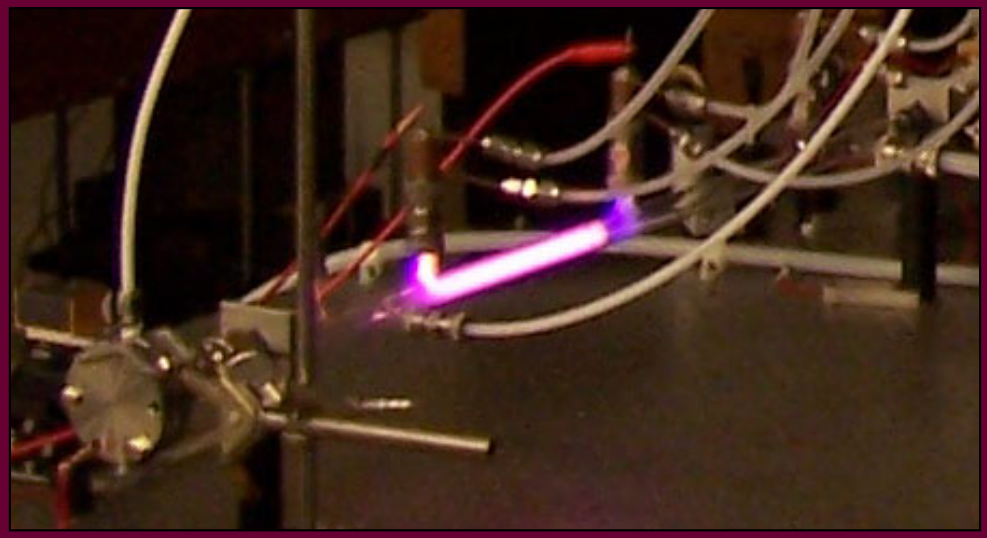

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The Meinel System of $^{14}N_2^+$

IR Auroral Emission Bands of N_2^+ observed by Meinel in 1950

YERKES OBSERVATORY
July 31, 1950

A NEW BAND SYSTEM OF N_2^+ IN THE INFRARED AURORAL SPECTRUM

Several strong auroral bands near 8000 A have been ascribed by Vegard and Kvifte[1] to members of the first positive system of N_2. Bates, Massey, and Pearse[2] have questioned this identification, in spite of apparent wave-length coincidences, because of the absence of other first positive bands from the particular vibrational levels.

Spectra obtained by the author with a relatively high resolution during the auroral storm of August 18 and 19, 1950, showed that the detailed structure of these bands was very different from first positive bands of N_2. The unidentified bands have two or more maxima, with a sharp edge on the violet side.

Conference on Auroral Physics University of Western Ontario, 1951

OSU MolSpec Abstract from 1951

INFRARED AURORAL EMISSION BANDS FROM THE $A^2\Pi$ STATE OF N_2^+ A7

A. B. Meinel
Yerkes Observatory
Williams Bay, Wisconsin

The author has recently identified six previously unidentified bands in the infrared auroral spectrum as arising from the $A^2\Pi$ state of N_2^+. The analysis of these bands, which appeared to be related from similarities in band profiles, gave vibrational constants for the lower state that were very close to those for the $X^2\Sigma$ state of N_2^+. A systematic discrepancy of a few wave numbers was noted which cannot be explained by observational errors, but which may be due to progressive changes in rotational structure from band to band. The doublet structure of these bands is very similar to the same transition in CN. A re-examination of the relative band intensities indicates that the $A^2\Pi$ state of N_2^+ lies at 8997 cm^{-1}. An observational test of this identification would be provided by the requirement of a strong band at 9189 A and a weaker band at 9470 A in the auroral spectrum.

The Meinel ($A^2\Pi_u$-$X^2\Sigma_g^+$) System of N_2^+

ν' \ ν''	0	1	2	3	4	5	6
0	9016	6841	4699	2590	513	-1530	-3540
1	10889	8715	6572	4463	2387	343	-1666
2	12733	10558	8416	6306	4230	2187	177
3	14546	12371	10229	8120	6043	4000	1990
4	16329	14155	12013	9903	7827	5783	3774
5	18083	15908	13766	11656	9580	7537	5527
6	19806	17631	15489	13380	11303	9260	7250
7	21500	19325	17183	15073	12967	10953	8944
8	23163	20988	18846	16737	14660	12617	10607
9	24797	22622	20480	18370	16294	14251	12241
10	26400	24226	22083	19974	17897	15854	13845
11	27974	25799	23657	21548	19471	17428	15418
12	29518	27343	25201	23092	21015	18972	16962
13	31032	28858	26715	24606	22529	20486	18477

Dalby and Douglas first characterized the N_2^+ Meinel system in the laboratory in 1951 (Phys. Rev. 84).

Calculated
Experimental

10200 – 10600 cm^{-1} diode laser

Adapted from Tarsitano & Oka *J. Mol. Spec.* 219, 2003.

The First Positive Group ($B^3\Pi_g - A^3\Sigma_g^+$) of N_2

ν' \ ν''	0	1	2	3	4	5	6	7	8	9
0	9512	8079	6674	5297	3947	2625	1332			
1	11217	9784	8379	7002	5652	4331	3037	1772	535	
2	12894	11461	10056	8678	7329	6007	4713	3448	2212	1004
3	14540	13108	11703	10326	8976	7654	6361	5096	3859	2681
4	16160	14727	13321	11944	10594	9273	7979	6714	5477	4270
5	17749	16316	14911	13513	12184	10862	9668	8303	7067	5859
6	19309	17876	16471	16093	14742	12422	11129	9862	8627	7419
7	20840	19407	18002	16625	16274	13963	12660	11395	10158	8960
8		20909	19504	18126	16777	16455	14161	12896	11670	10462
9			20976	19599	18249	26927	16612	14369	13132	11924
10				21041	19692	18310	17076	16811	14575	13307
11					21105	19873	18489	17224	15988	14780
12						21166	19873	18607	17370	16163

First observed in the visible
by Deslandres in 1902
(C. R. Society, Paris, 134)

Calculated
Experimental

10200 – 10600 cm^{-1}
diode laser

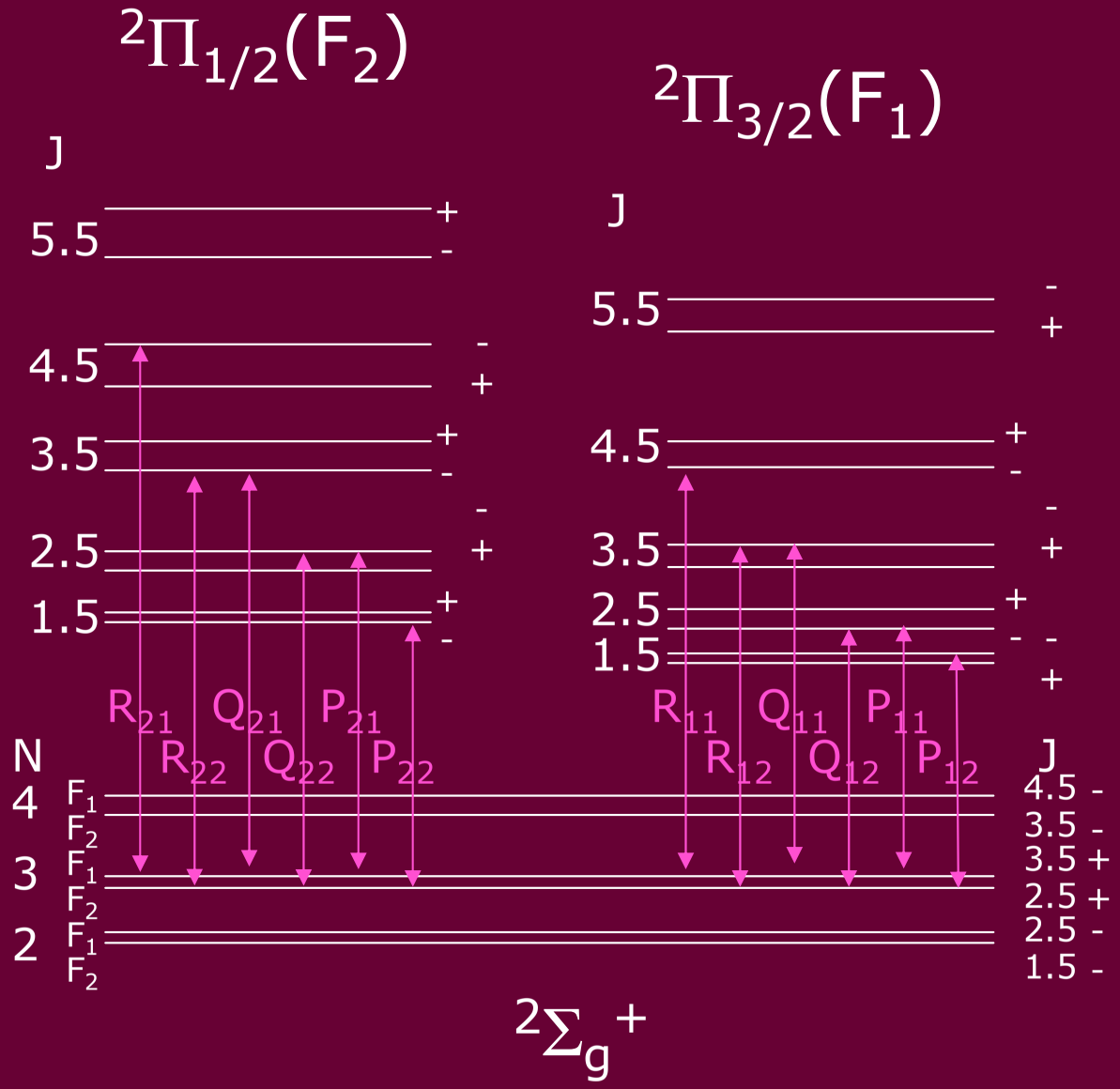
Adapted from Dieke & Heath *Johns Hopkins Spec. Report 17*, 1959
& Roux & Michaud *J. Mol. Spec.* 97, 253, 1983.

The $A^2\Pi_u$-$X^2\Sigma_g^+$ System of $^{14}N_2^+$

The $A^2\Pi_u$ state displays Λ-doubling and Hund's case a applies.

The $X^2\Sigma_g^+$ state of N_2^+ is split by spin-rotation interaction. Hund's case b applies.

P, Q, and R-type vibronic transitions are allowed.



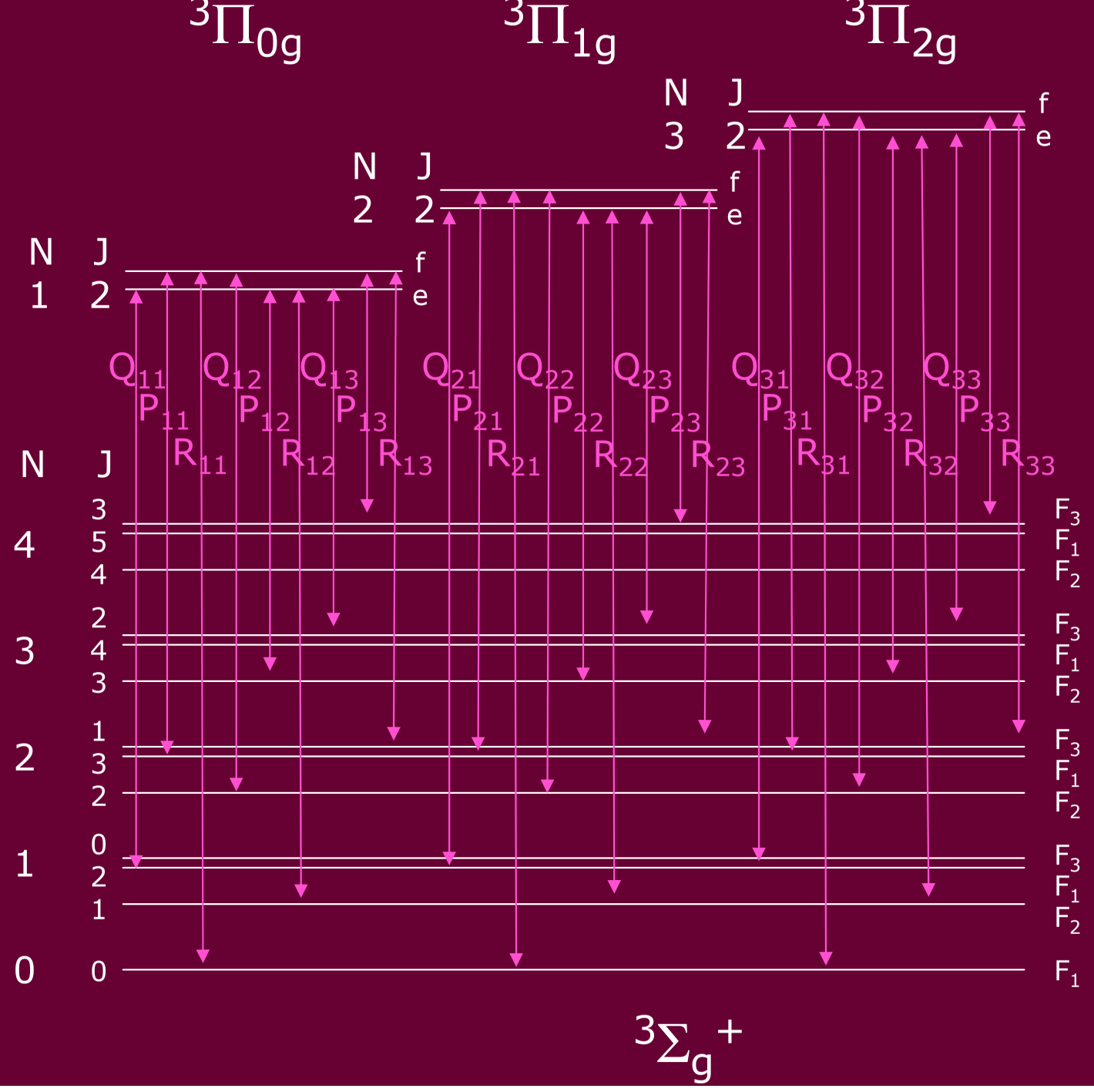
The $B^3\Pi_g - A^3\Sigma_g^+$ System of N_2

Hund's case a applies for the $B^3\Pi_u$ state at low J, and an intermediate between Hund's cases a and b applies at high J.

The $^3\Pi_g$ state is split into 6 sub-states

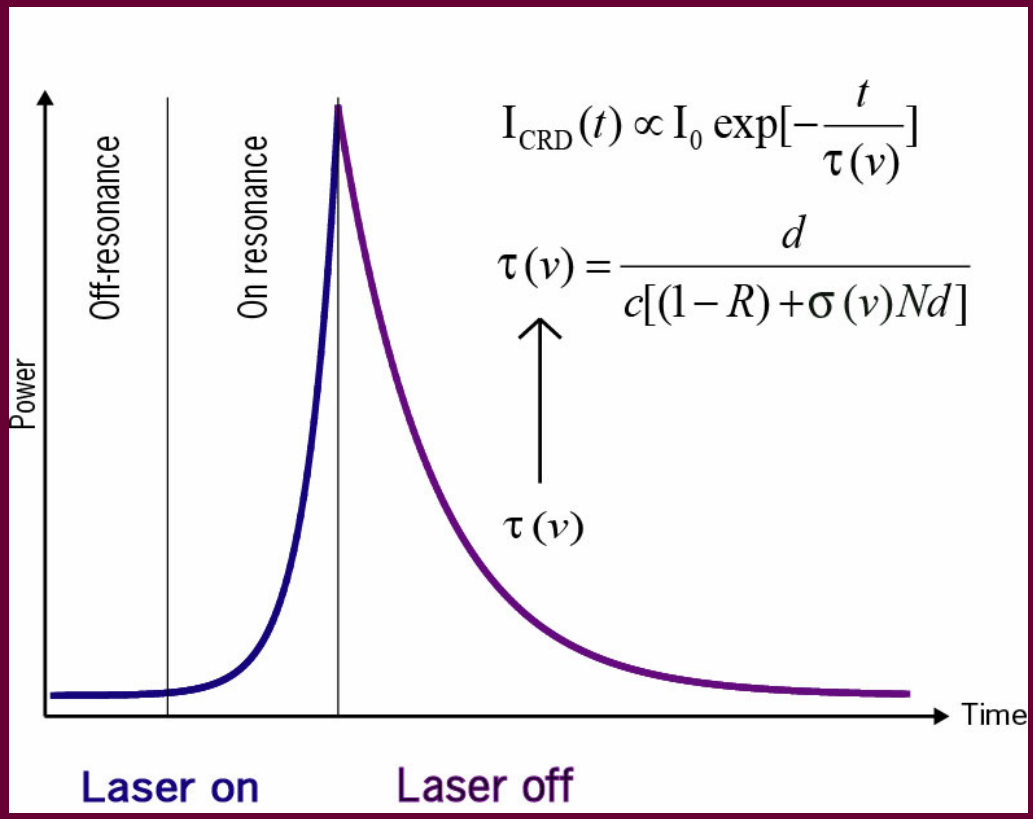
Hund's case b applies for the $A^3\Sigma_g^+$ state.

P, Q, and R-type vibronic transitions are allowed.



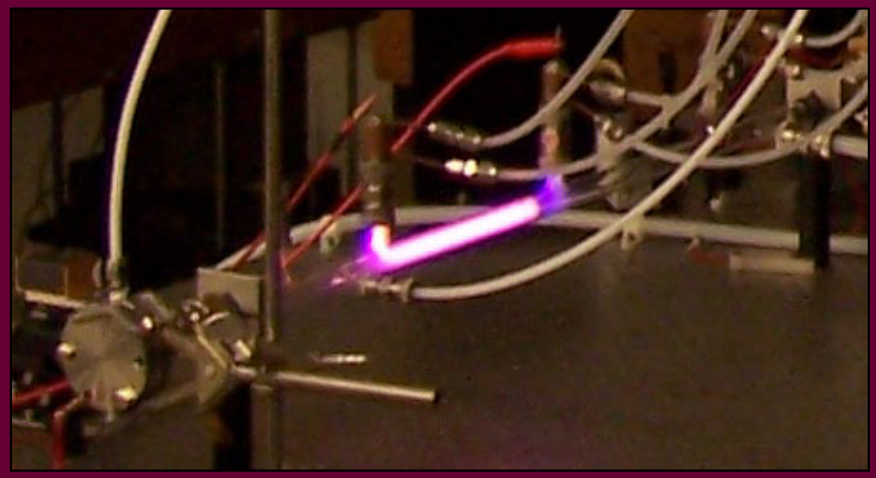
CW Cavity Ringdown Spectroscopy (cw-CRDS)

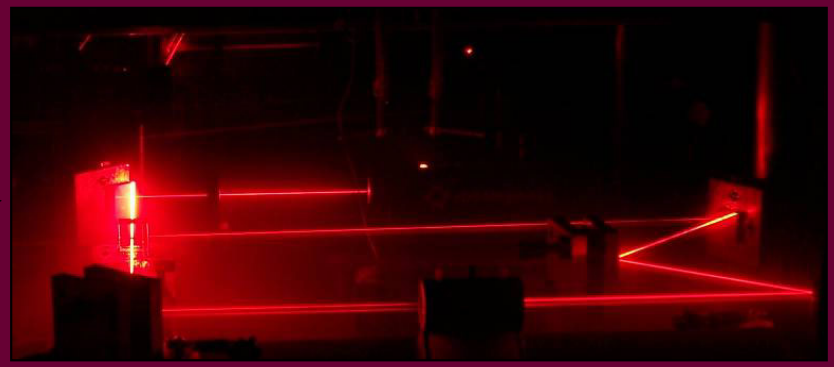
- A high finesse cavity is placed around the discharge.
- Laser light is coupled into the cavity, which is cycled in and out of resonance.

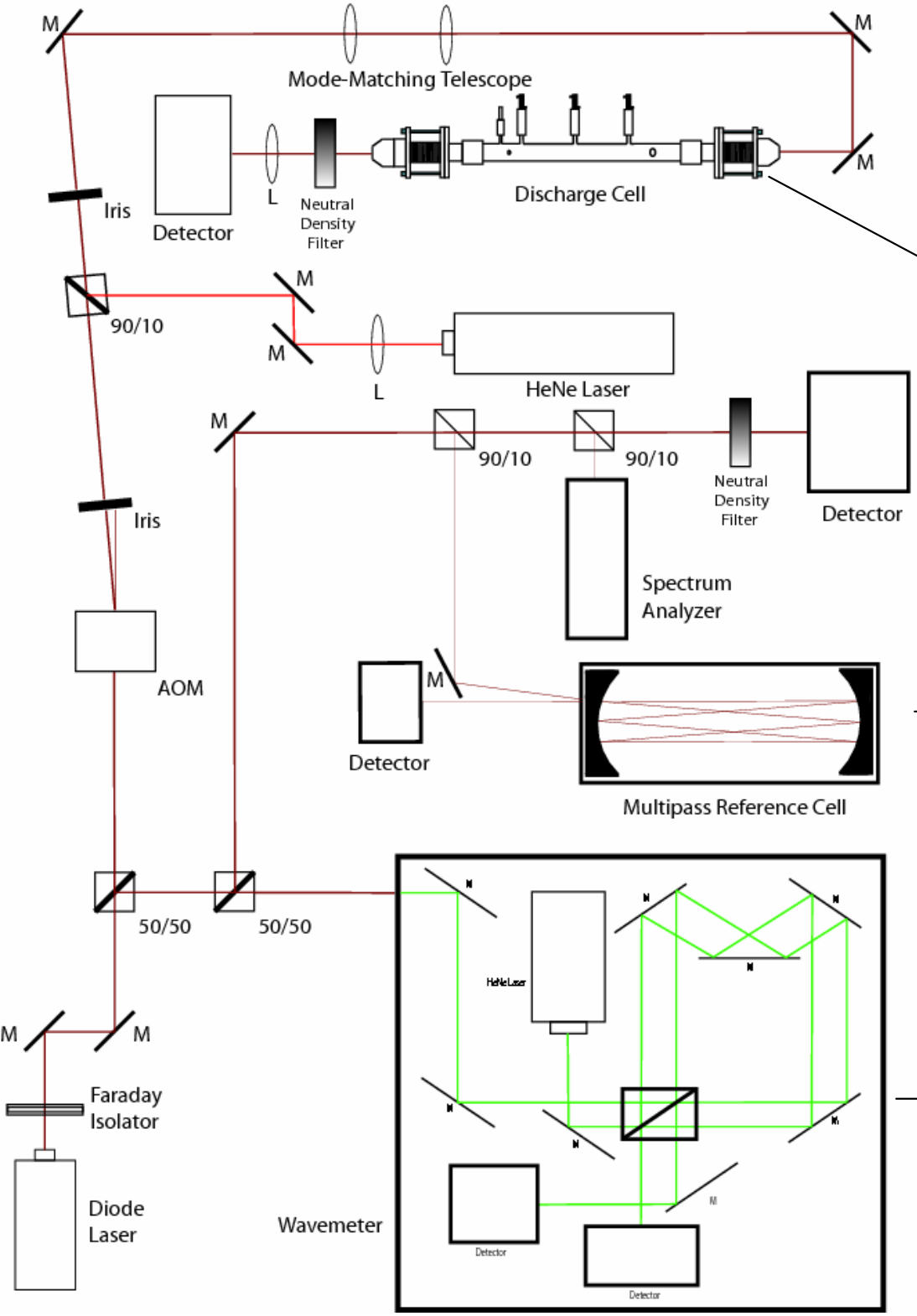


- When the cavity is on resonance the laser light is diverted or switched off.
- The exponential decay rate is a direct measurement of absorption.

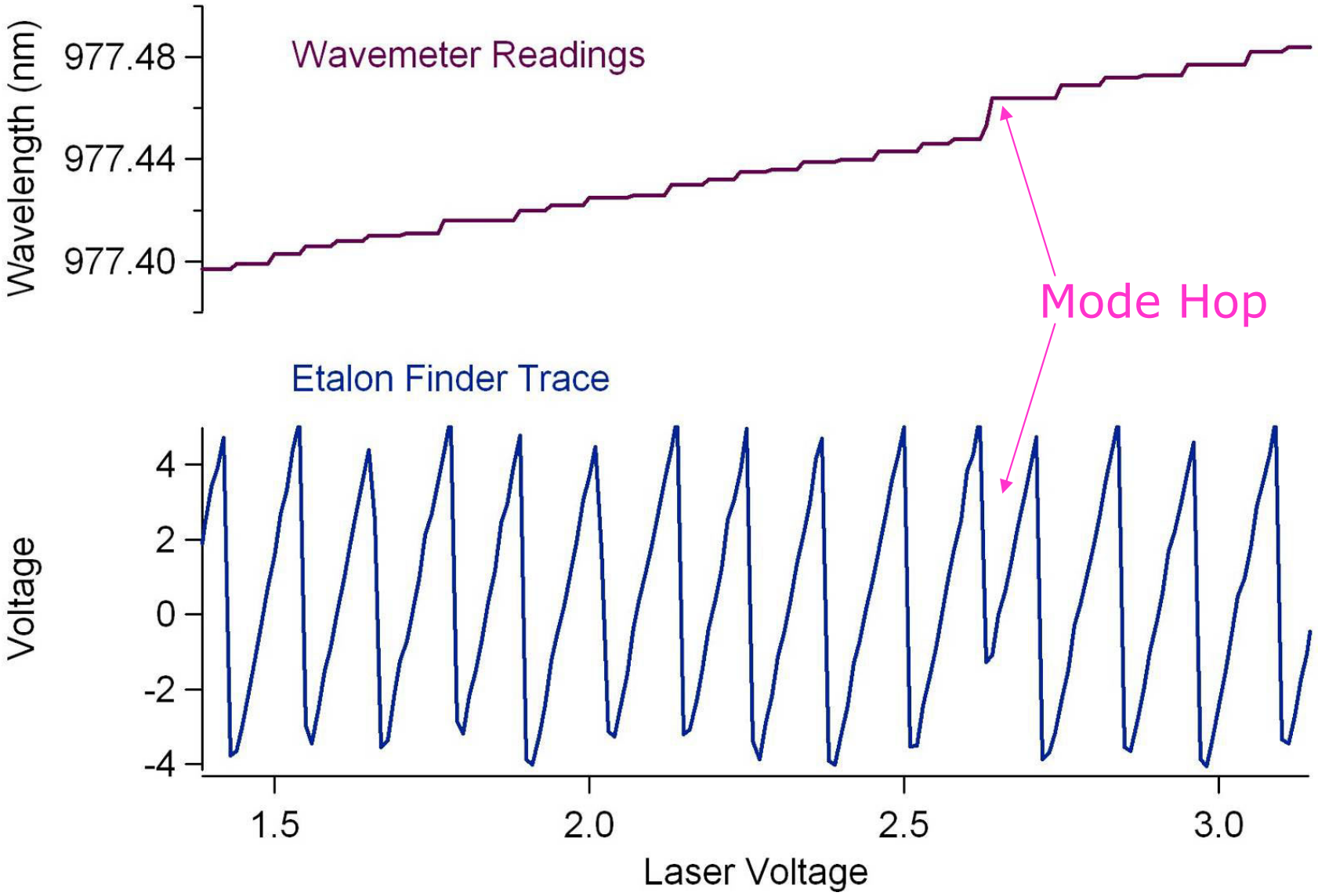
Experimental Setup



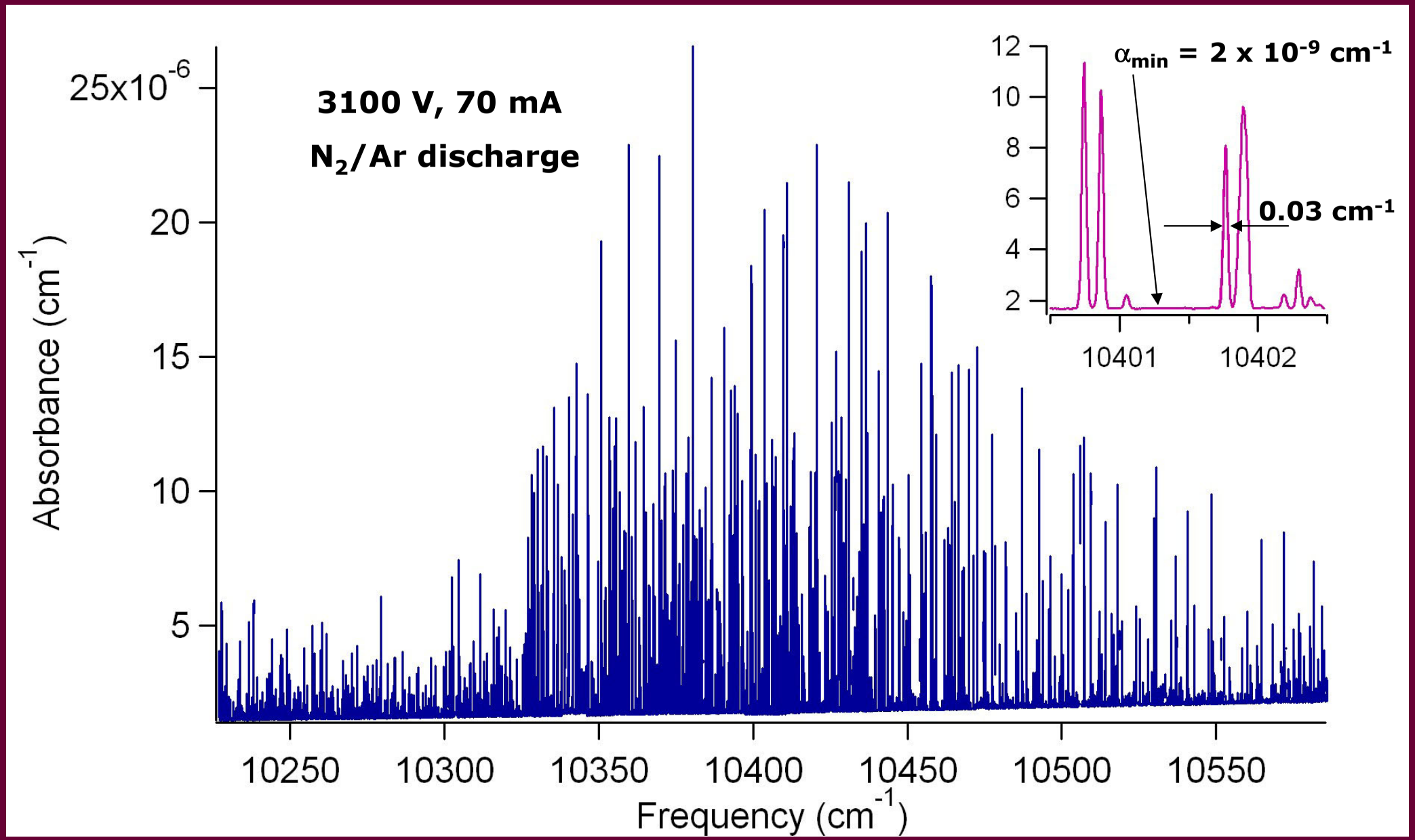




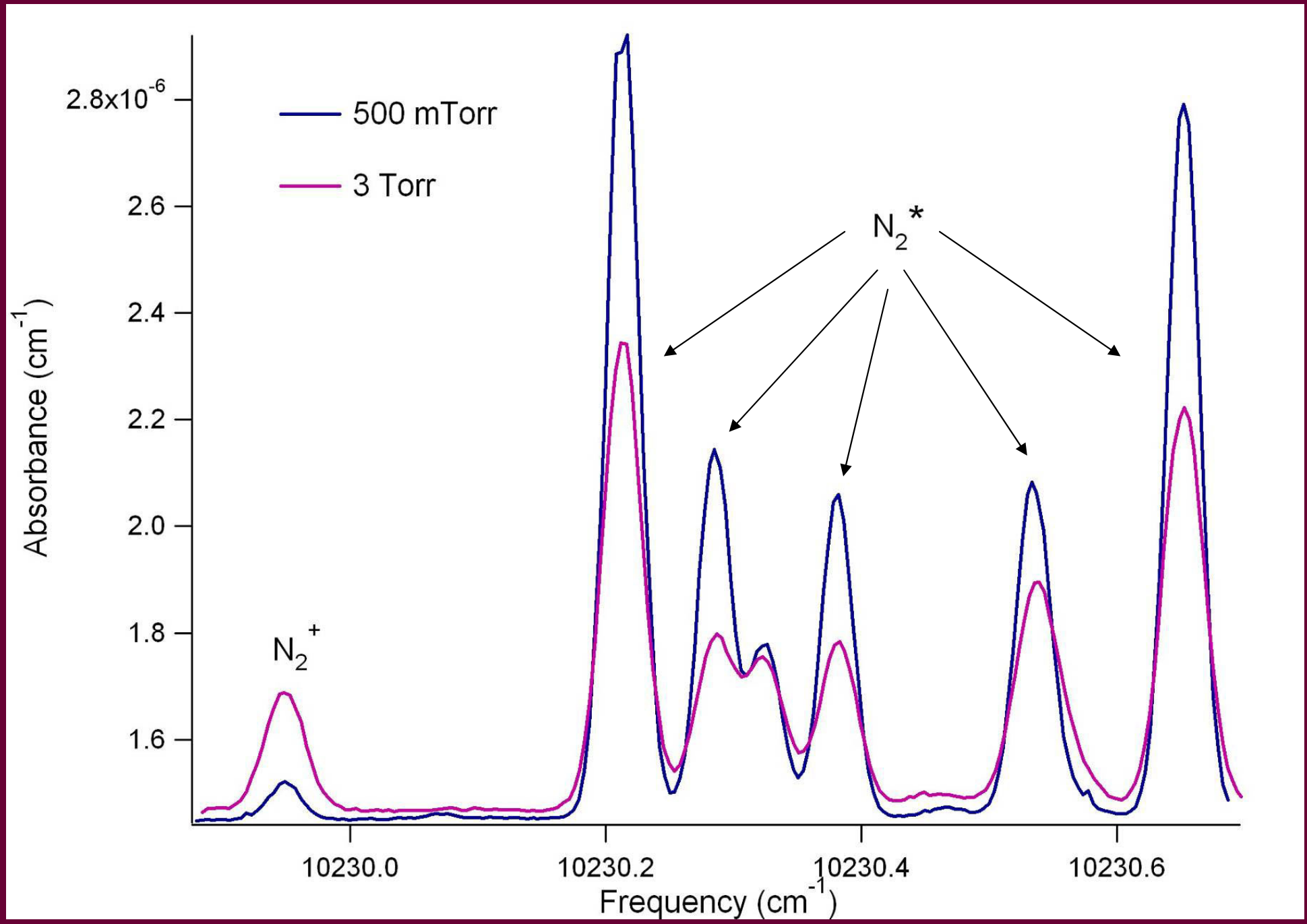
Spectral Calibration



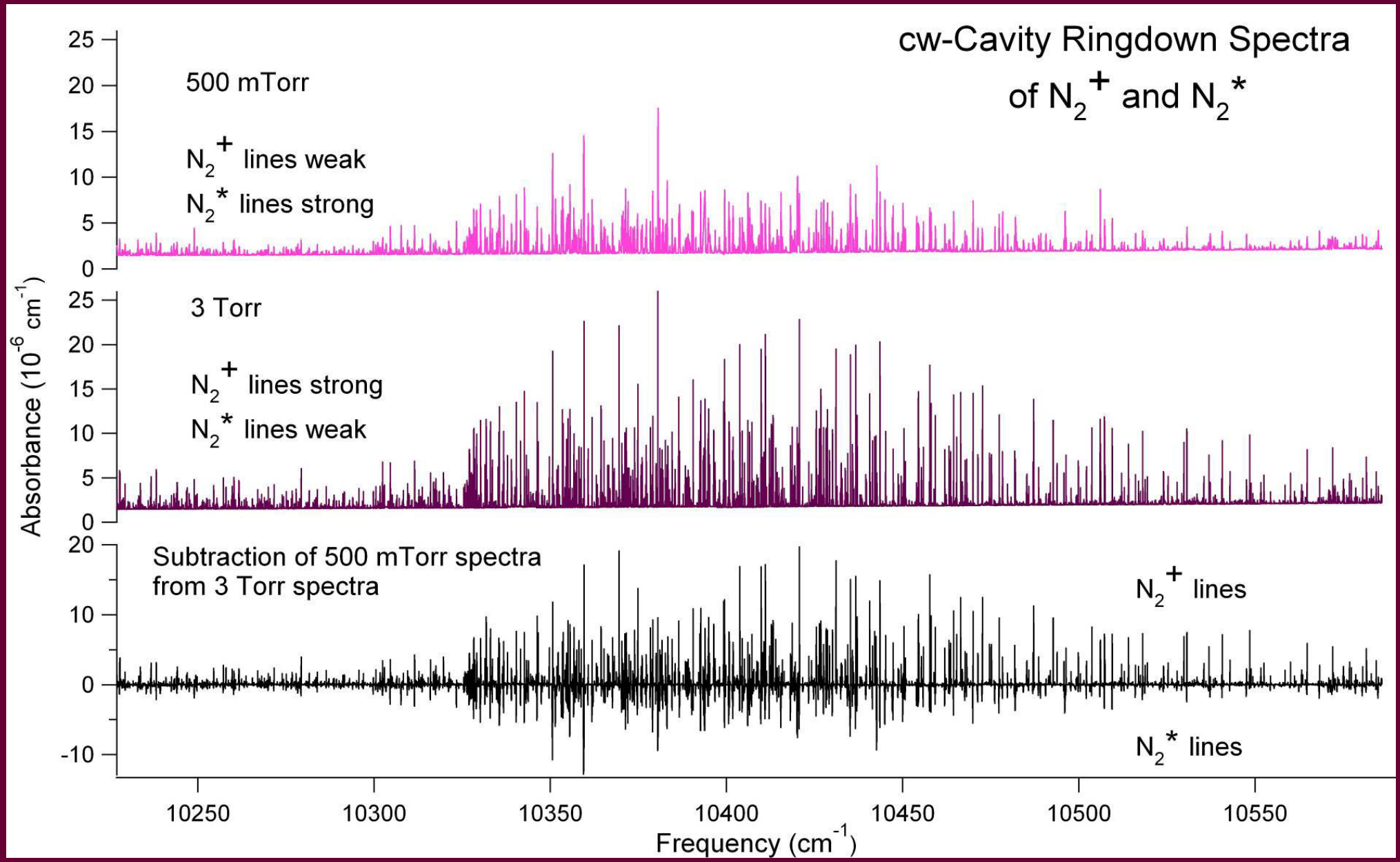
The N_2^+ Spectrum



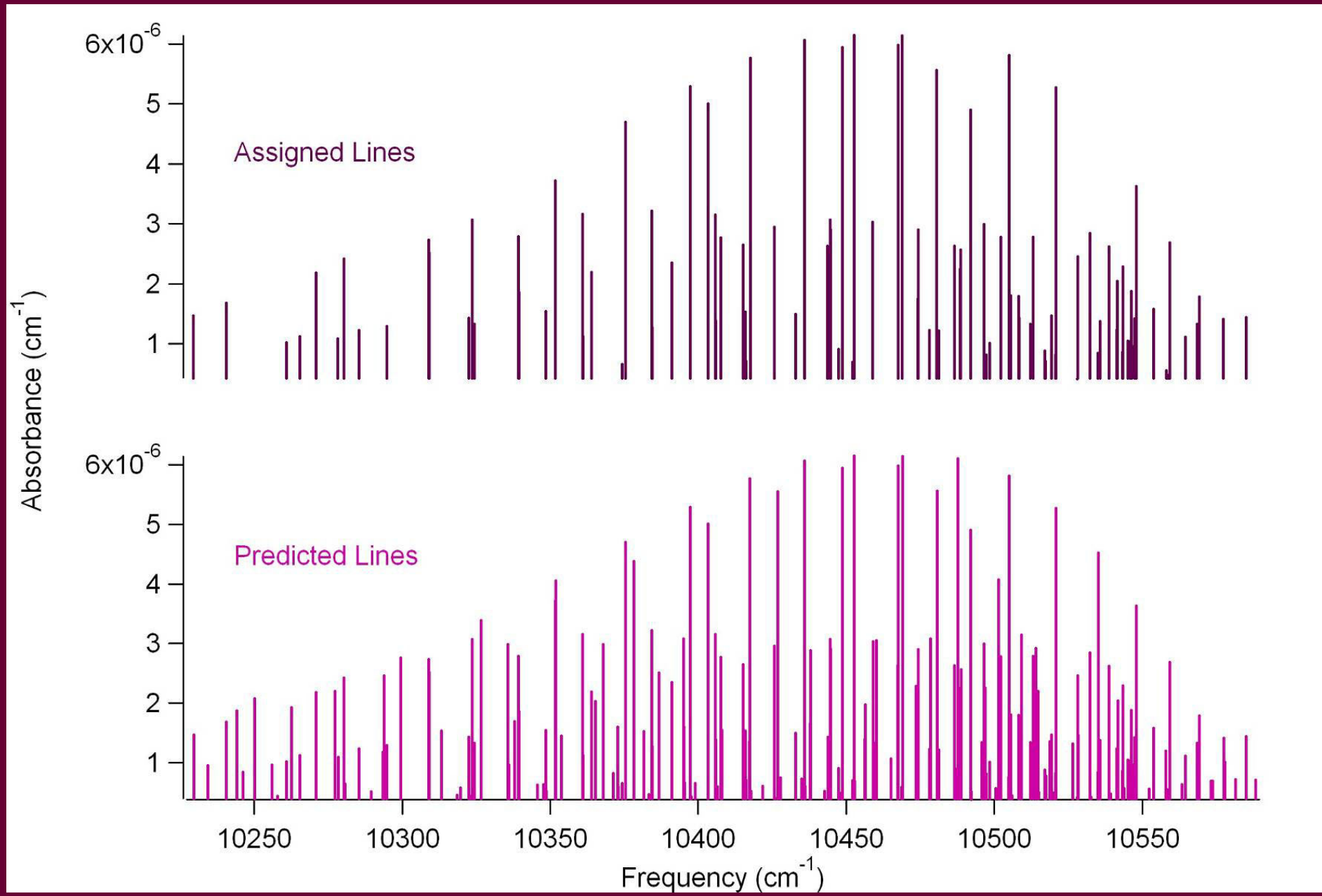
N_2^* vs N_2^+


2.8x10^-6
2.6
2.4
2.2
2.0
1.8
1.6
Absorbance (cm^-1)
500 mTorr
3 Torr
N2*
N2+
10230.0
10230.2
10230.4
10230.6
Frequency (cm^-1)

The $A^2\Pi_u$-$X^2\Sigma_g^+$ System of $^{14}N_2^+$



$^{14}N_2^+$ Line Assignments



Frequencies calculated from Miller et al., *J. Chem. Phys.* 80, 1984 and Ferguson et al., *J. Mol. Spec.* 153, 1992.
Intensities calculated from Earls, *Phys. Rev.* 48, 1935.

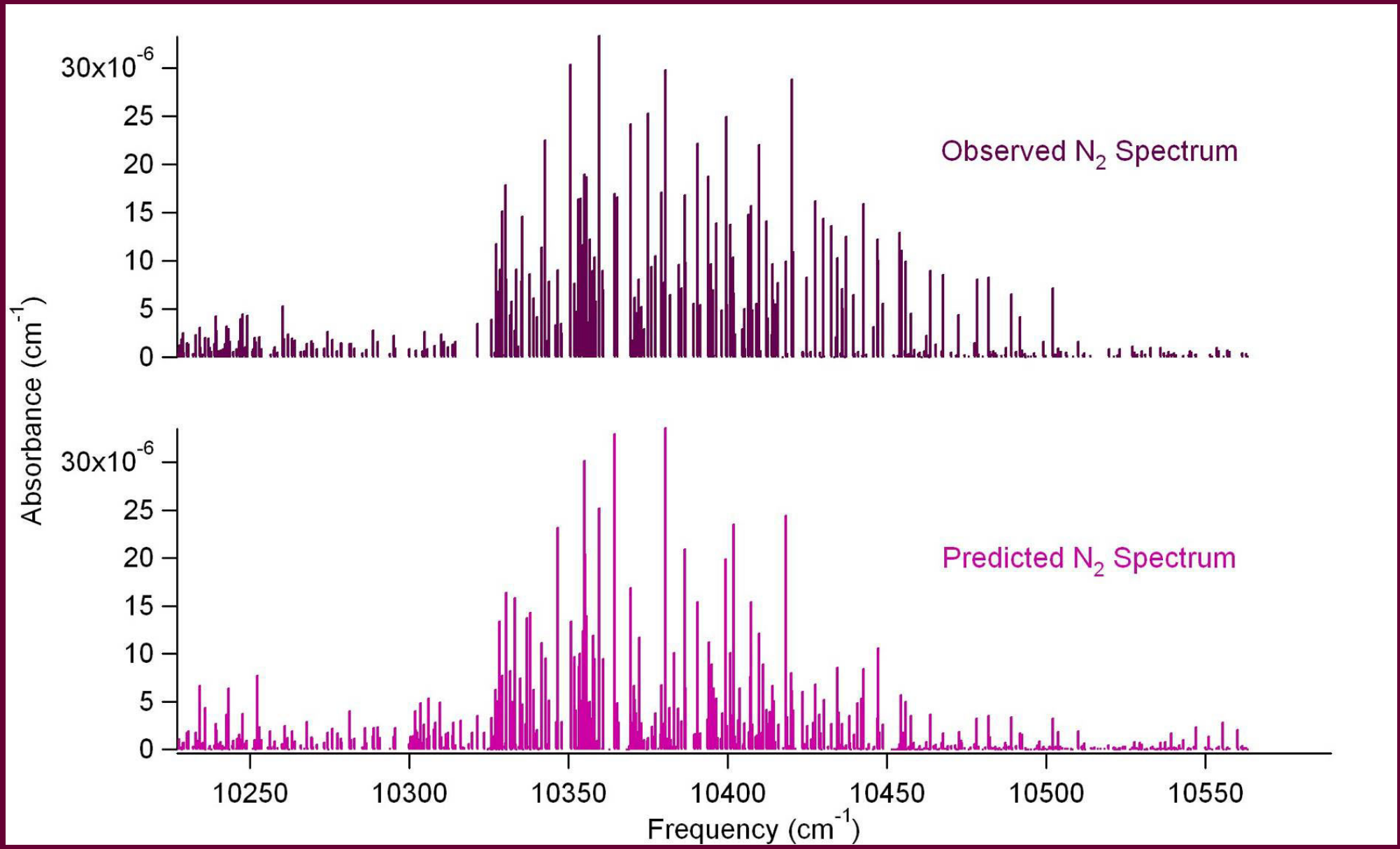
Spectral Parameters Determined for the $^{14}N_2^+$ 2-1 vibronic band

Parameter	Previous Studies†	Our Work
Upper State		
T_v	10558.1	10558.0931(25)
B_v	1.697391(67)	1.697442(87)
D_v	5.91(10) x 10^{-6}	5.952(75) x 10^{-6}
A_v	-74.6332(18)	-74.6417(43)
A_{dv}	-8.0(11) x 10^{-5}	-2.98(5) x 10^{-5}
q_v	-3.08(11) x 10^{-4}	-3.37(6) x 10^{-4}
p_v	4.87(27) x 10^{-3}	5.18(19) x 10^{-3}
Lower State		
B_v	1.903373(13)	1.903499(88)
D_v	5.942(8) x 10^{-6}	5.997(75) x 10^{-6}
γ	9.197(27) x 10^{-3}	9.31(54) x 10^{-3}

Fit RMS = 0.009 cm^{-1} for 95 lines

†Ho et al., *J. Mol. Spec.* 153, 1992
Ferguson et al., *J. Mol. Spec.* 153, 1992

The $^{14}N_2^*$ Problem



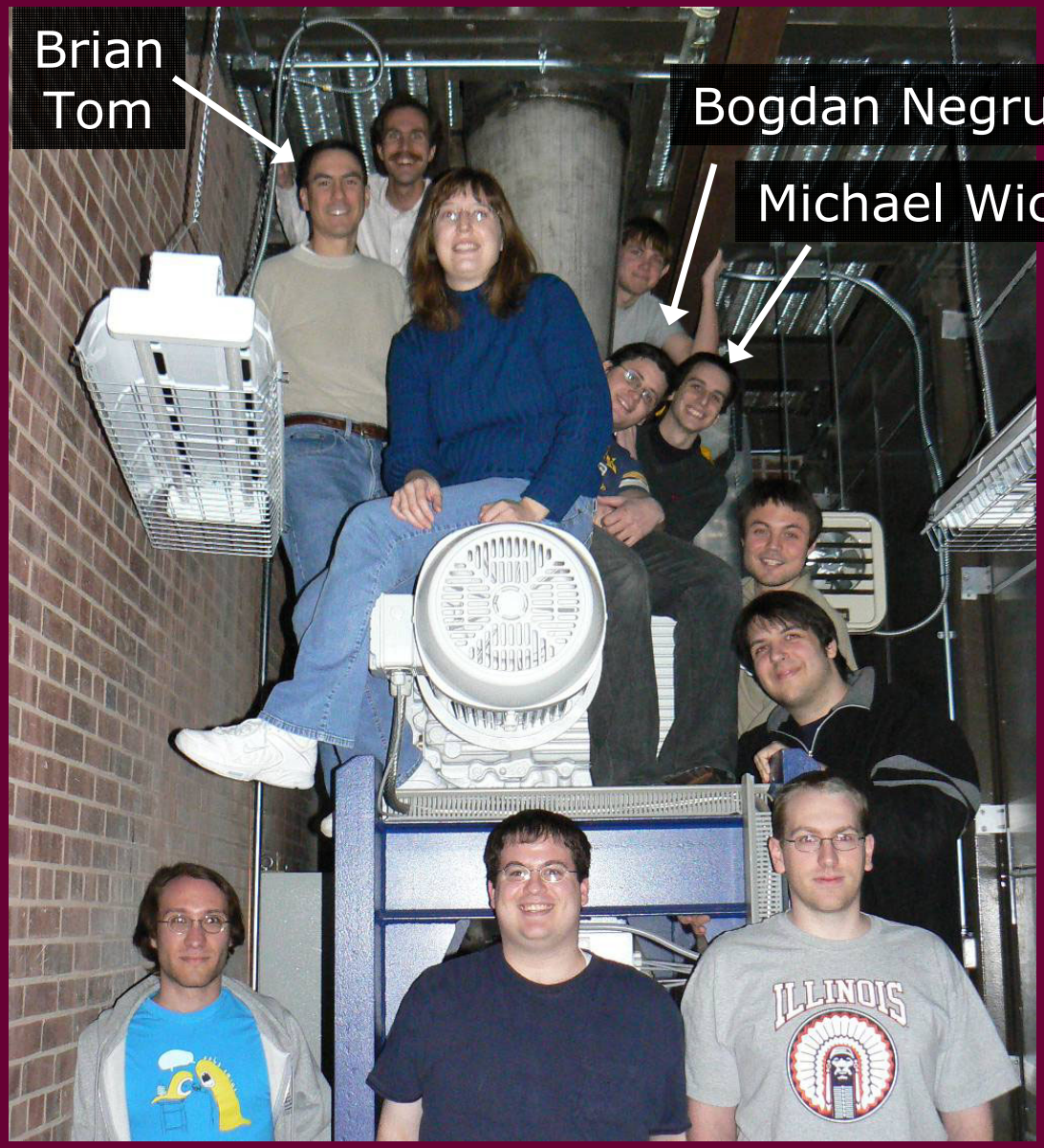
Frequencies calculated from Dieke and Heath *Johns Hopkins Spectroscopic Report* 17, 1959.

Intensities calculated from Budo, A. *Z. fuer Phys.* 105, 1937; Dieke and Heath *Johns Hopkins Spectroscopic Report* 17, 1959; Biloiu, Sun, Harvey, & Scime *J. of App. Phys.* 101, 2007.

Conclusions and Future Work

- The cw-CRDS spectra of N_2^+ and N_2^* from 10227 - 10590 cm^{-1} have been acquired.
- 95 N_2^+ lines from the 2-1 band of the Meinel system have been assigned and spectral parameters determined. More assignments are underway.
- $\geq$ 400 lines from the first positive band system of N_2^* have been identified. Final assignment and determination of spectral parameters is underway.
- Lines from the 3-2 band of the N_2^+ Meinel system may be observable.

Acknowledgments



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Josh DiGangi, Brian Pohrte,
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Christopher G.
Tarsitano for the
N_2^+ spectral fitting
routine

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