Line Strengths and Self-Broadening of Pure Rotational Lines of Carbon Monoxide and Nitrous Oxide Measured by Terahertz Time-Domain Spectroscopy

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Weston Aenchbacher[1], Mira Naftaly[2], and Richard Dudley[2]

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[1]Currently with Drexel University, Department of Electrical and Computer Engineering, Philadelphia, PA, USA

[2]National Physical Laboratory, Hampton Road,Teddington, Middlesex TW11 0LW, UK

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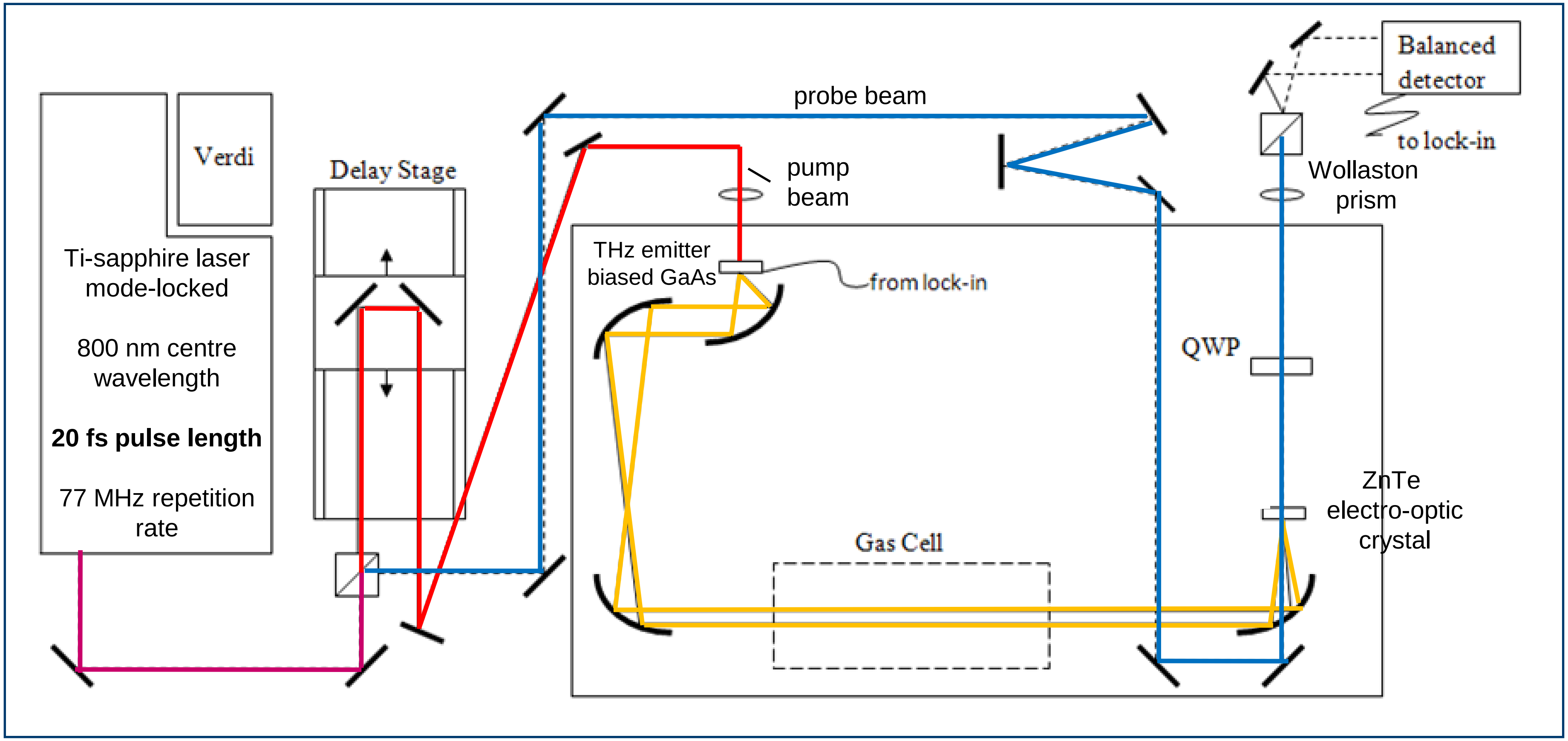
Introduction

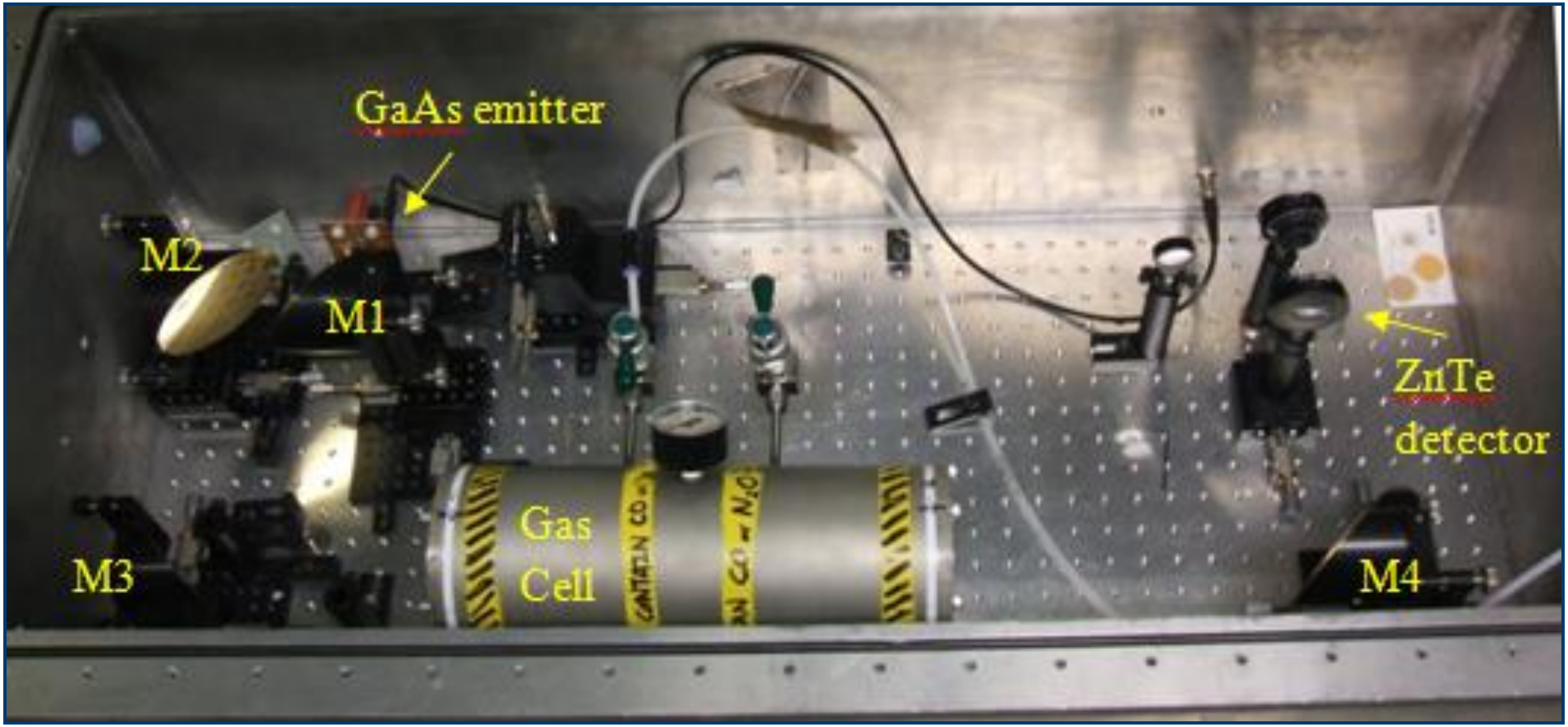
- NPL terahertz time-domain spectrometer (THz-TDS)
- CO Measurements and Results
  - Pure rotational lines from $J' = 3 \leftarrow 2$ to $J' = 22 \leftarrow 21$
  - Pressures of 0.7 – 5.1 bar
- N_2O Measurements and Results
  - Pure rotational lines from $J' = 10 \leftarrow 9$ to $J' = 53 \leftarrow 52$
  - Pressures of 0.7 – 1.2 bar

NPL Terahertz Time-Domain Spectrometer



- biased photoconductive emitter
- ZnTe refractive index proportional to THz E-field → rotates probe polarization

NPL Terahertz Time-Domain Spectrometer



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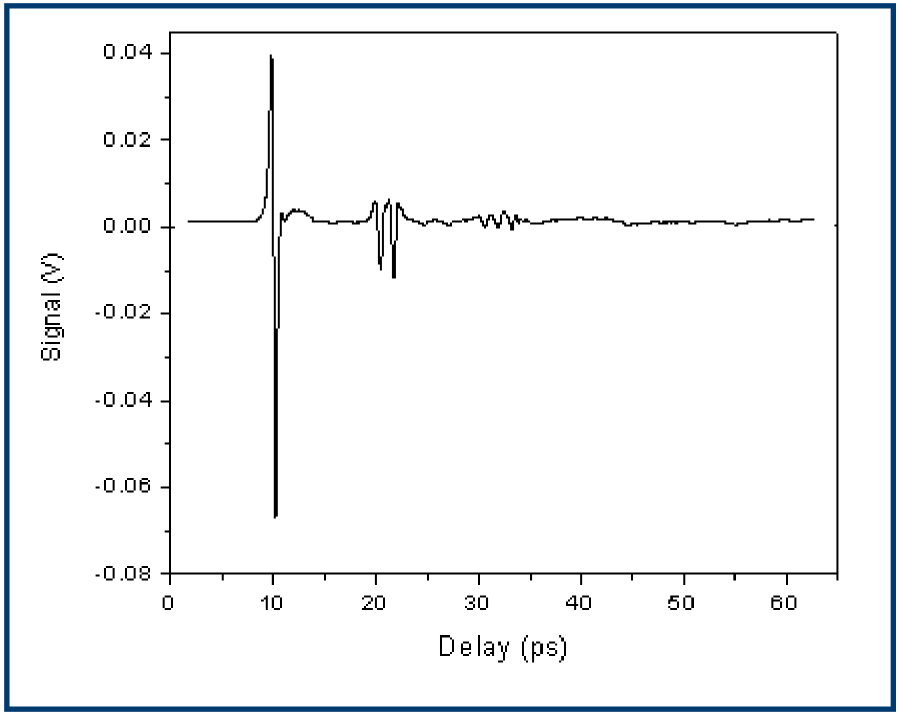
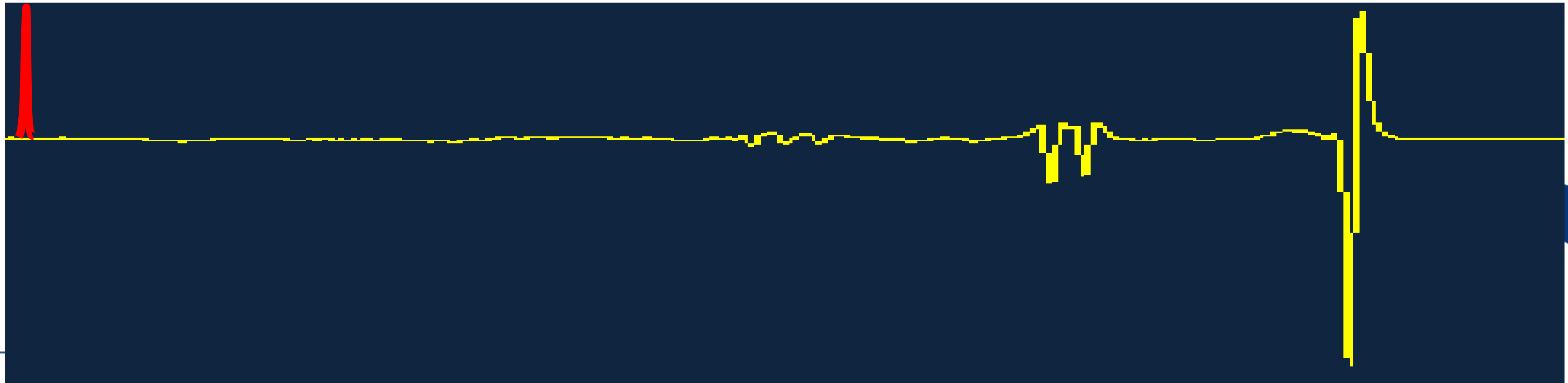
Time-Domain Measurement

- THZ pulse 20 ps
- Probe pulse 2 fs →
  ~delta function

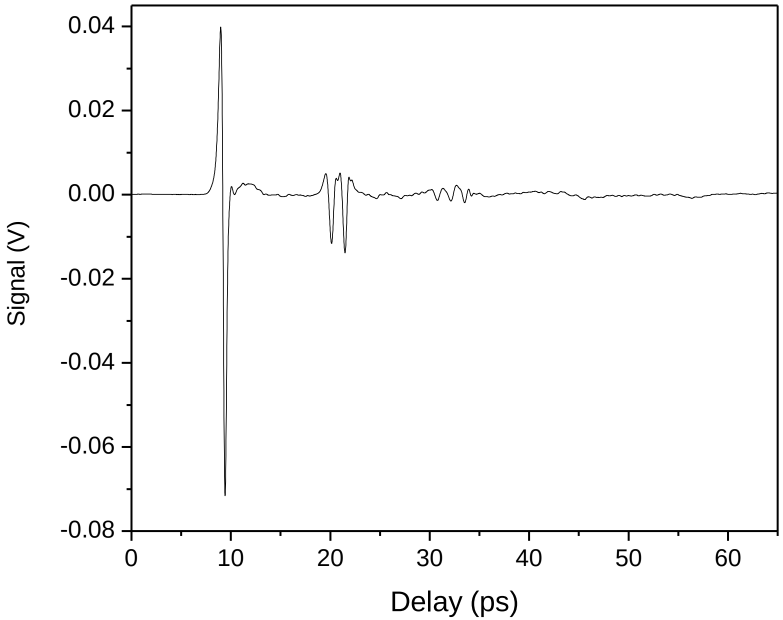


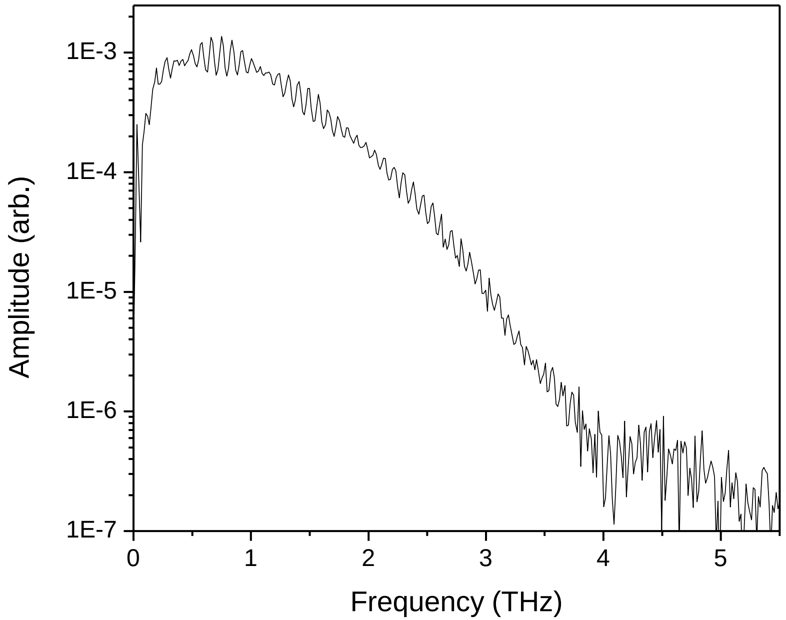
probe pulse ↙



THZ Spectrum

E-field in time —FFT→ Spectrum





$$\Delta f = \frac{1}{N\Delta t} = \frac{c}{2d} = 1.25\,\text{GHz}$$

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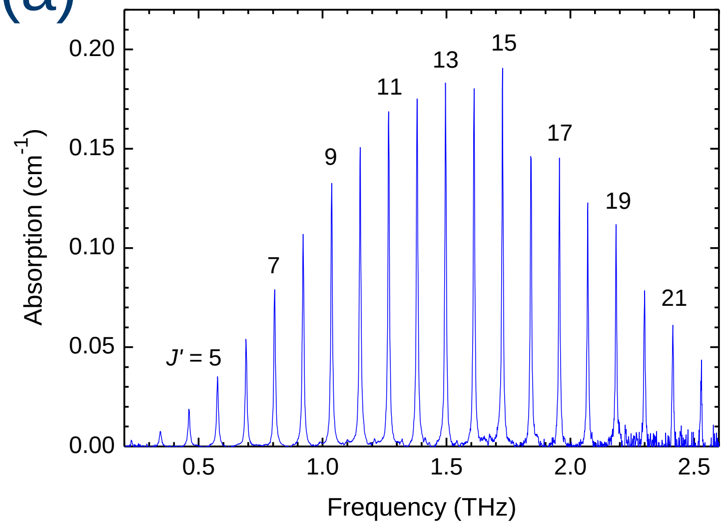
Sample CO Spectrum

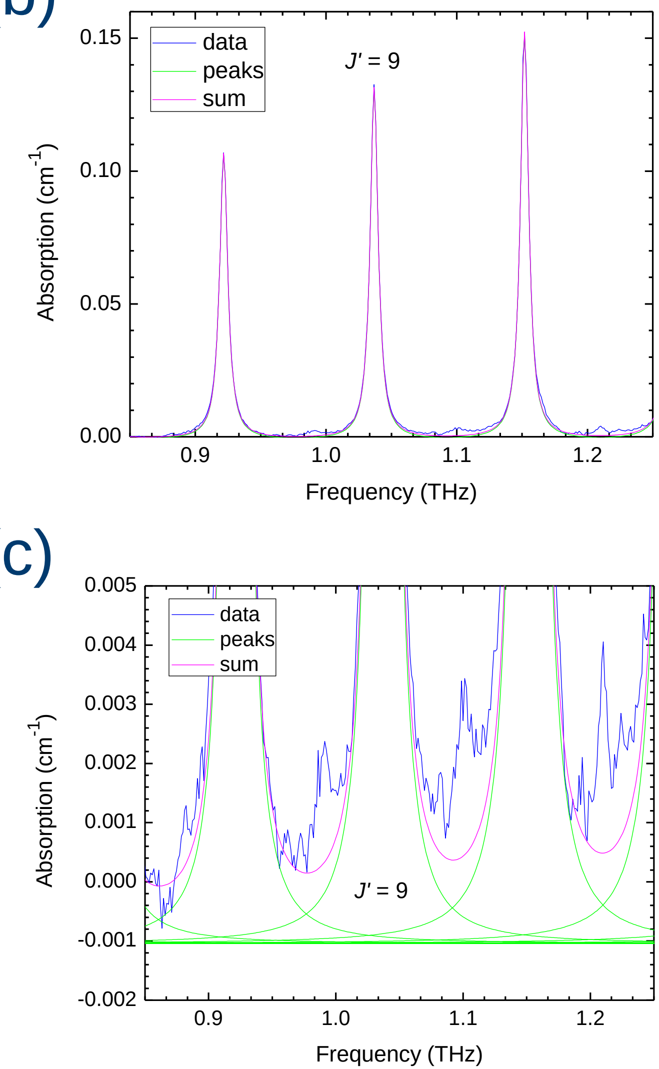
(a)



$$\sigma(\upsilon) = \frac{\alpha(\upsilon)}{N} = -\frac{2}{Nl}\ln\left(\frac{E_{CO}(\upsilon)}{E_0(\upsilon)}\right)$$

(b)

(c)



Lorentzian line shape assumed

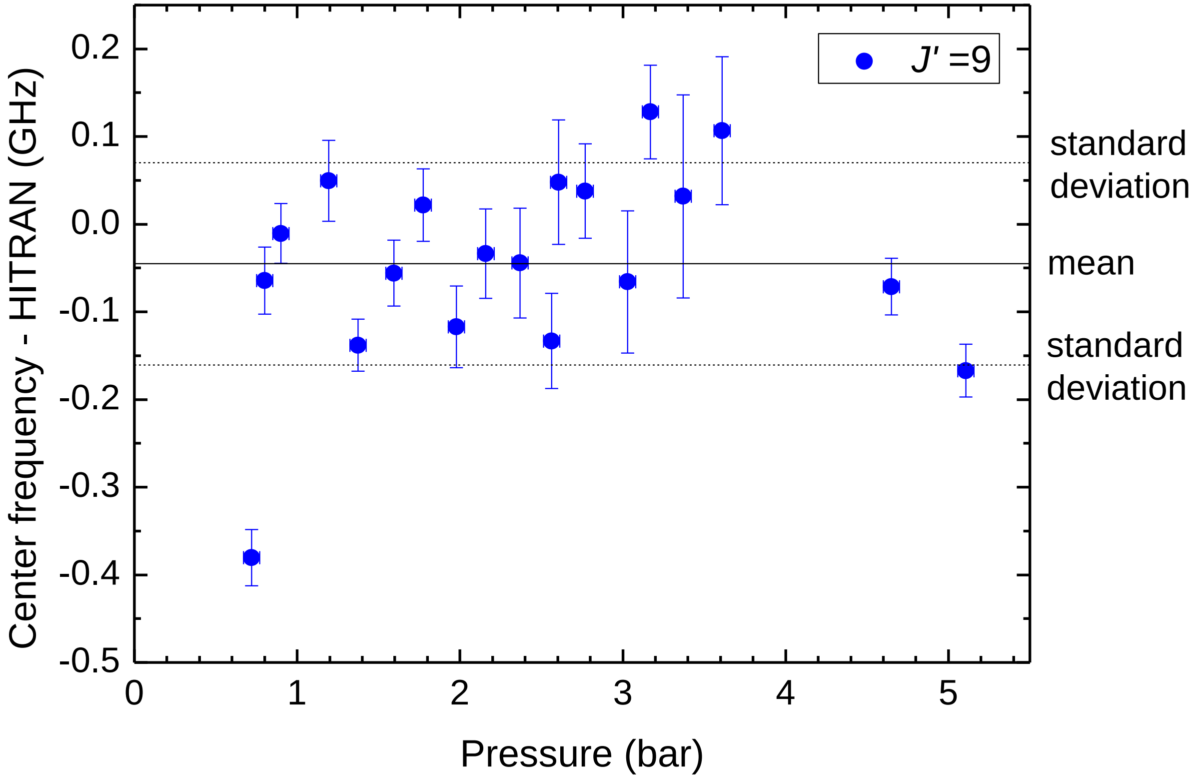
(a) CO absorption spectrum at 2 bar

(b) Section of sample fit at 2 bar

(c) Expanded section of fit at 2 bar

Line Center with Pressure, *J'* = 9 line

J' = 9 center frequency (minus HITRAN) vs. pressure



error bars → standard deviation

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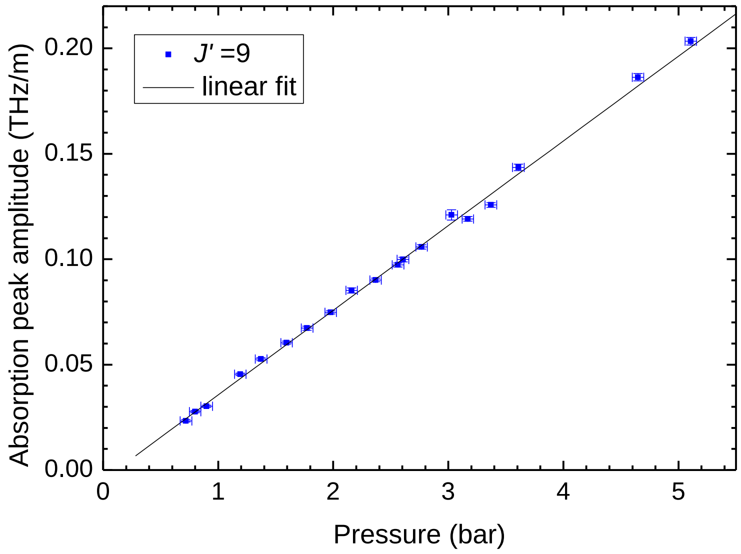
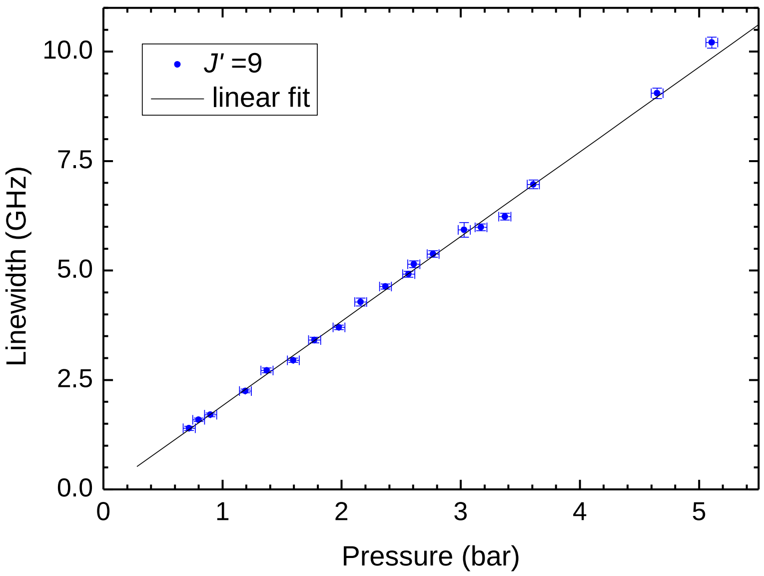
Sample Measurements, *J'* = 9 line

fit amplitude vs. pressure



$$S = kT \cdot \text{slope}$$

fit linewidth vs. pressure



$$\gamma self = \text{slope}$$

y error bars → standard deviation
x error bars → pressure uncertainty

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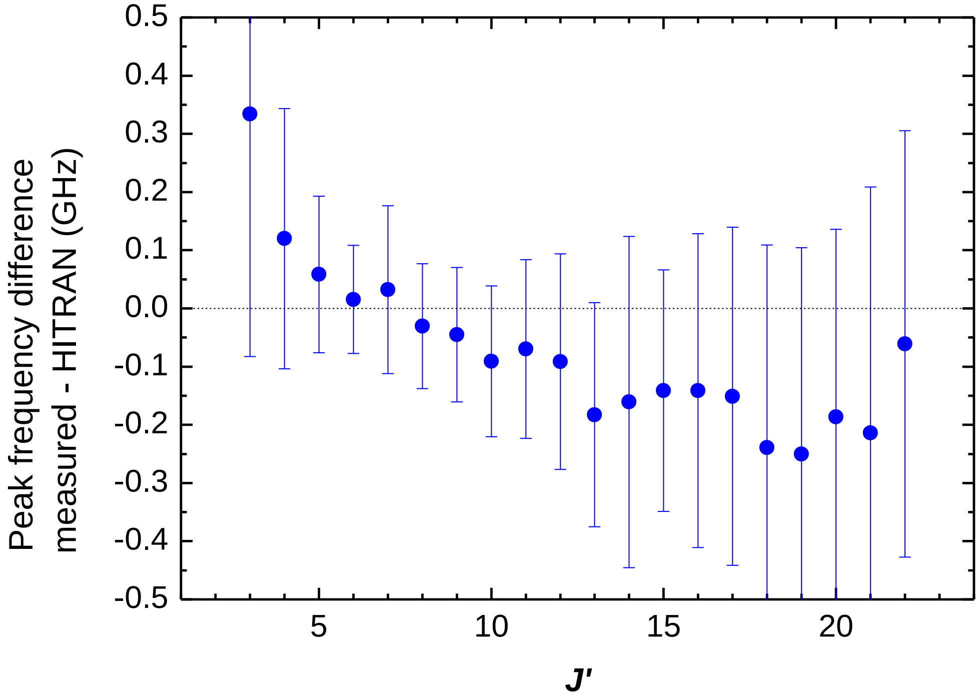
CO Line Center Frequencies

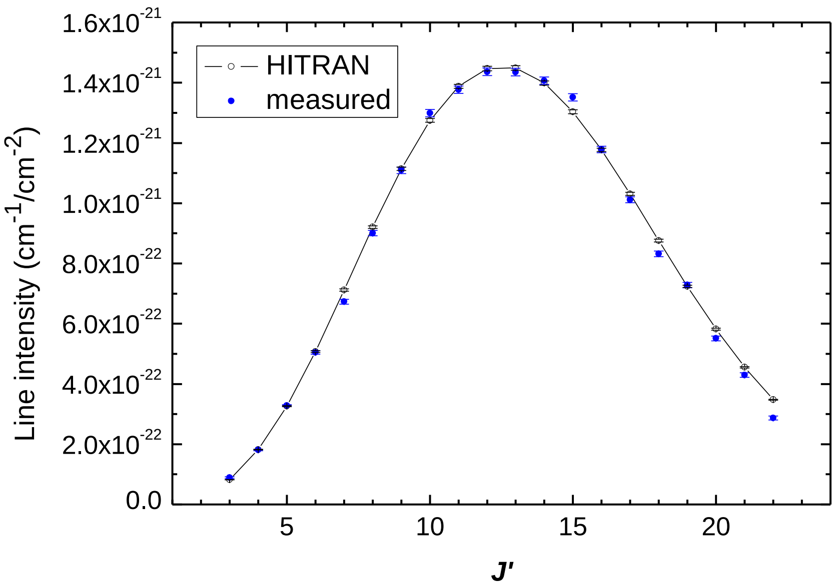
peak frequency (minus HITRAN) for *J'*



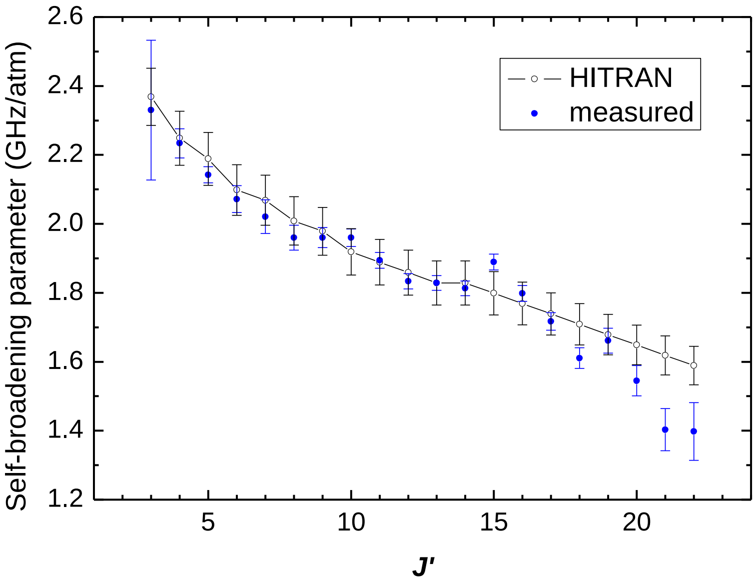
Peak frequencies are taken as average over all pressure measurements.

CO Results

Line Intensity for J'



Self-Broadening coefficient for J'



Tabulated data can be found:

W. Aenchbacher, M. Naftaly, and R. Dudley, "Line strengths and self-broadening of pure rotational lines of carbon monoxide measured by terahertz time-domain spectroscopy," Applied Optics 43/13, pp. 2490, 2010.

error bars → standard deviation

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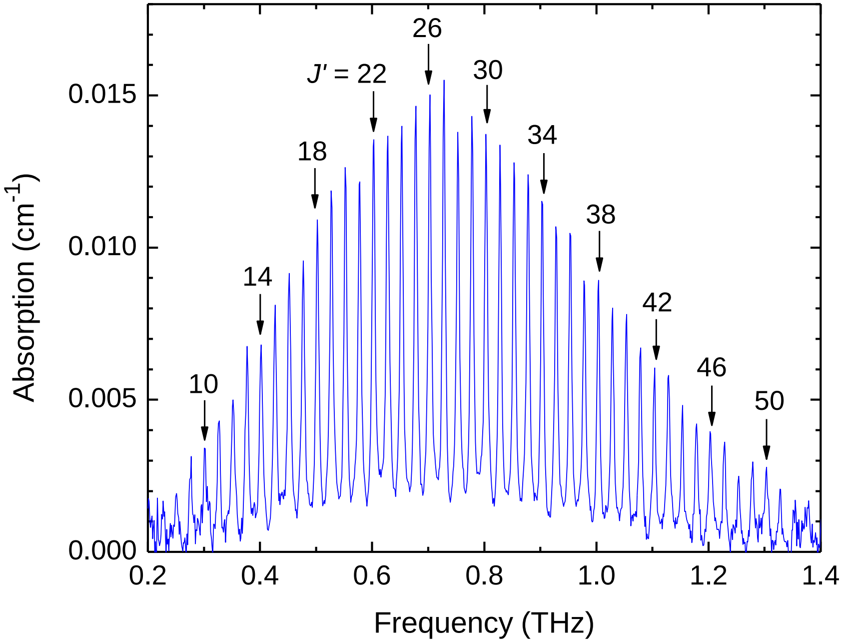
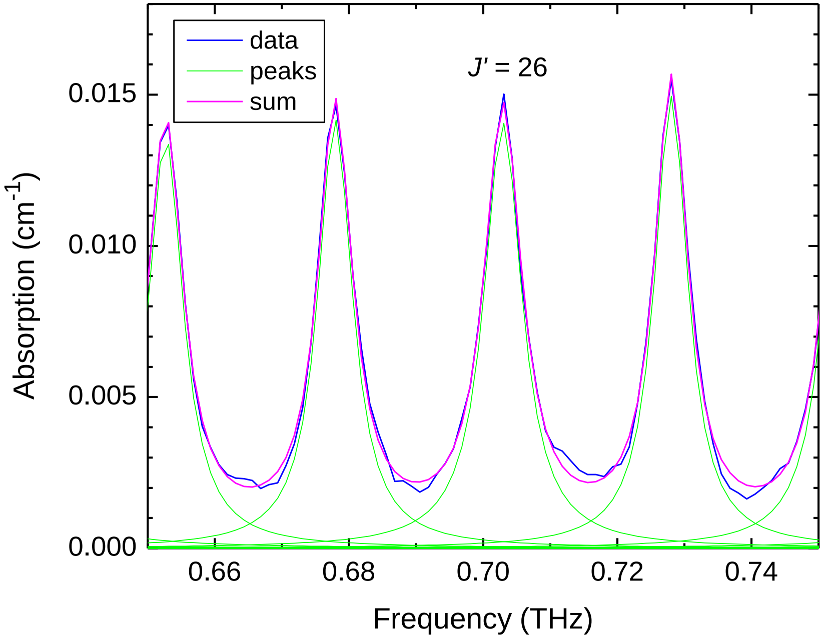
Sample N_2O Absorption Spectrum





(left) absorption spectrum at 1.2 bar

(right) section of sample fit at 1.2 bar

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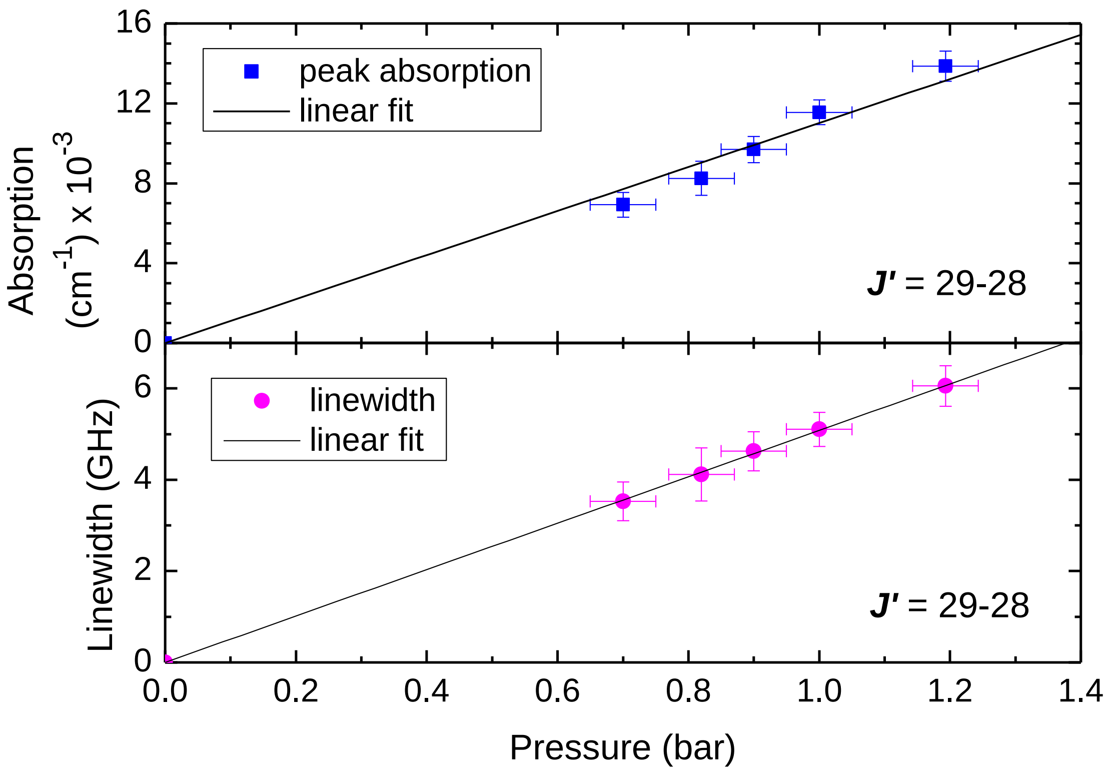
N_2O Sample Measurements, *J'* = 29 line



- (top) absorption fit amplitude vs. pressure
- (bottom) fit linewidth vs. pressure
- vertical 95% confidence bars, horizontal pressure uncertainty
- zero point included to decrease fit uncertainty

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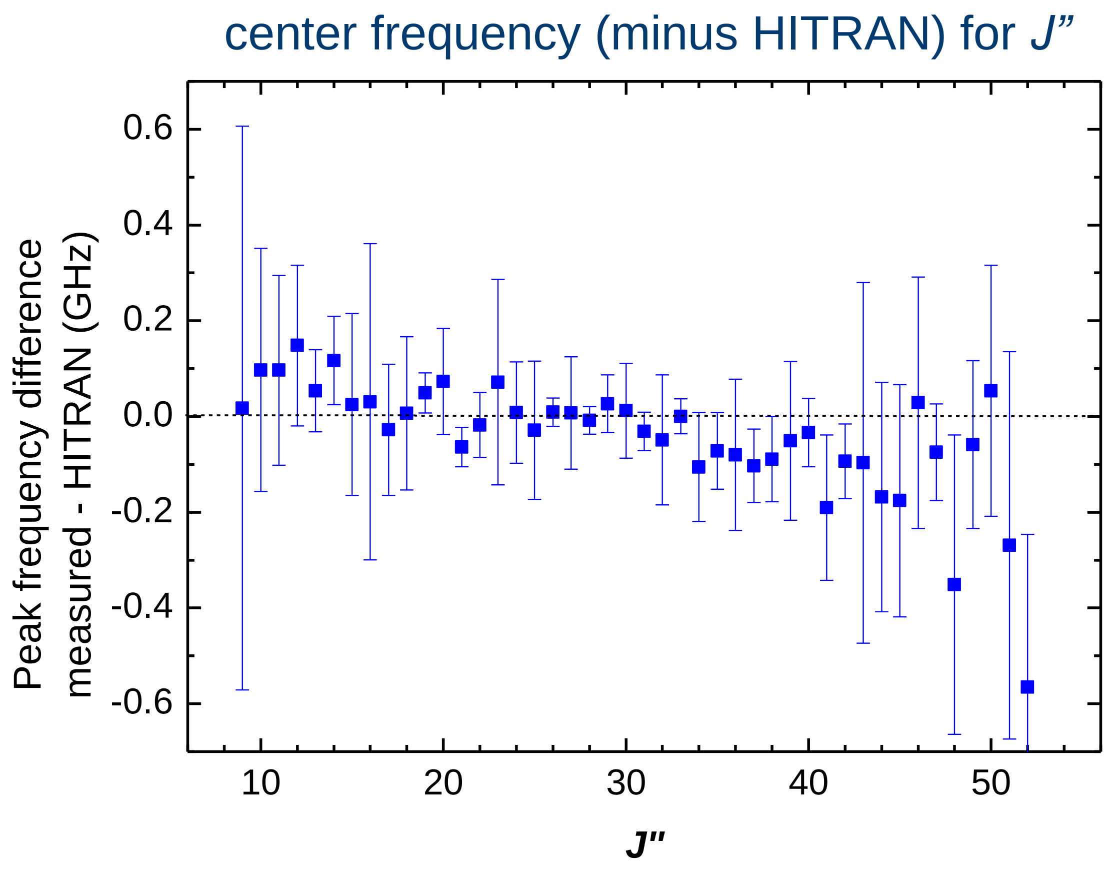
N_2O Line Center Frequencies



error bars → 95% confidence interval

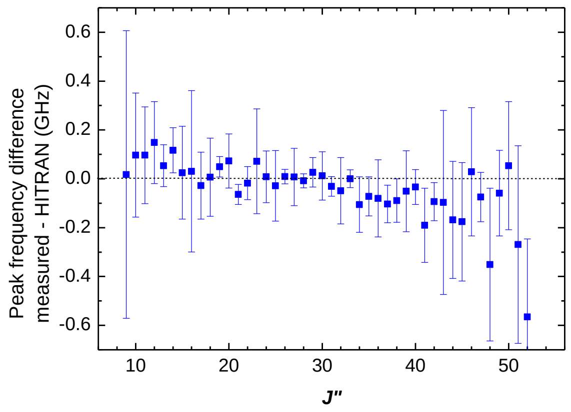
N_2O Parameters Calculated

Eqn. 1

$$\nu_0 = 2B(J+1)$$

Eqn. 2

$$\alpha_0 = CB^3(J+1)^3 \exp[-(h/kT)BJ(J+1)]$$



Parameter		This work	From literature
B	From line frequencies & Eq. 1	**12.53 ± 0.08 GHz** **0.418 ± 0.03 cm^{-1}**	0.419 cm^{-1} [a,b]
	From line intensities & Eq. 2	**12.3 ± 0.2 GHz** **0.410 ± 0.008 cm^{-1}**	
Electric dipole moment μ_0		–0.155±0.003 D	-0.161 D [b,c]

(a) E.D. Palik, K.N. Rao, "Pure rotational spectra of CO, NO, and N_2O between 100 and 600 microns", *J. Chem. Phys.*, **25**/6 (1956) 1174-1176.

(b) F. Rohart, J.-M. Colmont, G. Wlodarczak, J.-P. Bouanich, "N_2- and O_2-broadening coefficients and profiles for millimeter lines of $^{14}N_2O$", *J. Mol. Spectr.*, **222** (2003) 159-171.

(c) L. Nguyen, J. Buldyreva, J.-M. Colmont, F. Rohart, G. Wlodarczak, E.A. Alekseev, "Detailed provile analysis of millimeter 502 and 602 GHz N_2O-$N_2(O_2)$ lines at room temperature for collisional linewidth determination", *Mol. Phys.*, **104** (2006) 2701-2710.

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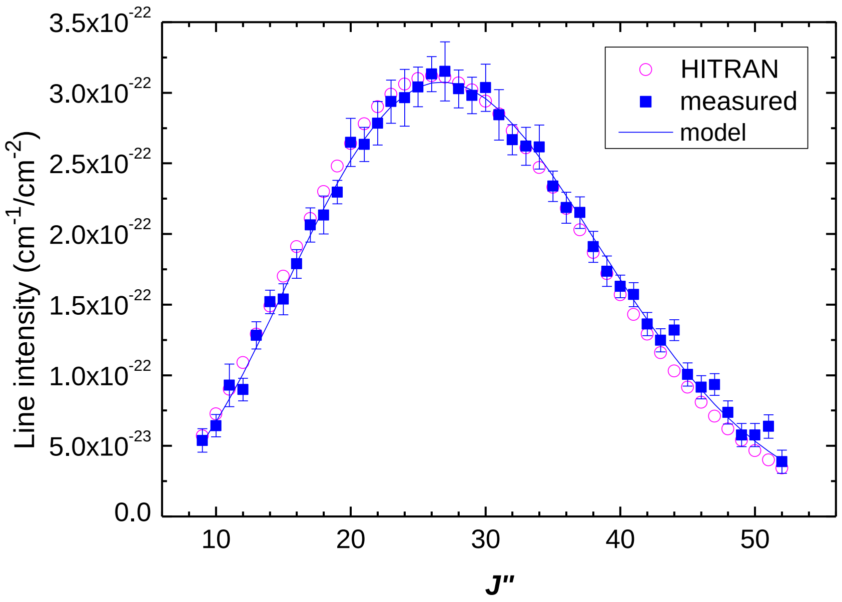
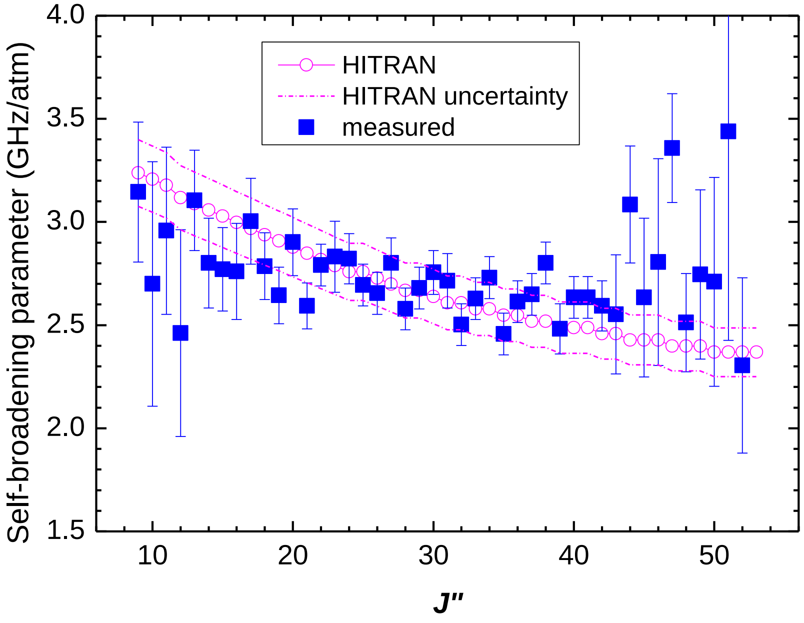
N_2O Results

line intensity vs. *J"*



self-broadening coefficient vs. J"



Tabulated data available soon:

W. Aenchbacher, M. Naftaly, and R. Dudley, "Line strengths and self-broadening of pure rotational lines of nitrous oxide measured by terahertz time-domain spectroscopy," JOSA B. (submitted May 2010).

error bars → 95% confidence interval

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Conclusion

- THz TDS demonstrated as a viable tool for measurement of molecular spectra.
- Contribution to knowledge base of CO molecule
  - Measured intensity and self-broadening with THz-TDS for the first time
- Contribution to knowledge base of N2O molecule
  - Measurements to fill gaps in available experimental data for intensity and self-broadening

Thank You

For more information:

- W. Aenchbacher, M. Naftaly, and R. Dudley, “Line strengths and self-broadening of pure rotational lines of carbon monoxide measured by terahertz time-domain spectroscopy,” Applied Optics 43/13, pp. 2490, 2010.
- W. Aenchbacher, M. Naftaly, and R. Dudley, “Line strengths and self-broadening of pure rotational lines of nitrous oxide measured by terahertz time-domain spectroscopy,” JOSA B. (submitted May 2010).

- Weston Aenchbacher: wla24@drexel.edu
- Mira Naftaly: mira.naftaly@npl.co.uk

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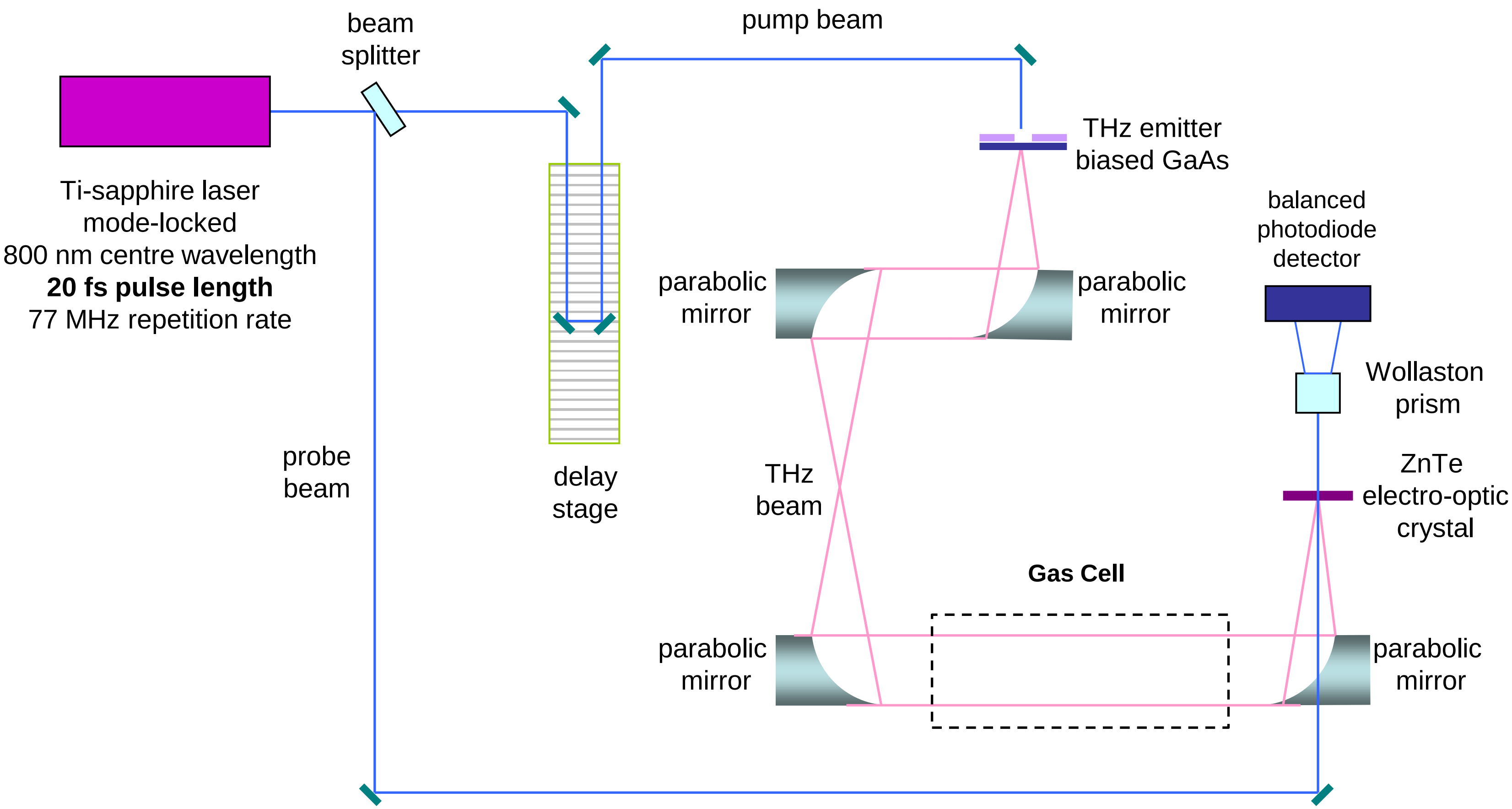
NPL Terahertz Time-Domain Spectrometer



- biased photoconductive emitter
- ZnTe refractive index proportional to THz E-field (Pockels Effect) → rotates probe polarization

CO Tabulated Results

	Line Intensities $((cm^{-1}/molecule.cm^{-2}) \times 10^{-22}$			Self-Broadening (GHz/atm)		
$J' \leftarrow J''$	Measured	Standard Deviation	HITRAN	Measured	Standard Deviation	HITRAN
$3 \leftarrow 2$	0.89	0.02	0.821 ± 0.008	2.33	0.10	2.37 ± 0.08
$4 \leftarrow 3$	1.81	0.02	1.82 ± 0.02	2.23	0.02	2.25 ± 0.08
$5 \leftarrow 4$	3.28	0.02	3.262 ± 0.03	2.14	0.01	2.19 ± 0.08
$6 \leftarrow 5$	5.05	0.05	5.075 ± 0.05	2.07	0.02	2.10 ± 0.07
$7 \leftarrow 6$	6.76	0.06	7.117 ± 0.07	2.02	0.02	2.07 ± 0.07
$8 \leftarrow 7$	9.00	0.07	9.206 ± 0.09	1.96	0.02	2.01 ± 0.07
$9 \leftarrow 8$	11.09	0.09	11.14 ± 0.11	1.96	0.01	1.98 ± 0.07
$10 \leftarrow 9$	12.99	0.09	12.75 ± 0.12	1.96	0.01	1.92 ± 0.07
$11 \leftarrow 10$	13.77	0.10	13.88 ± 0.14	1.89	0.01	1.89 ± 0.07
$12 \leftarrow 11$	14.36	0.10	14.47 ± 0.14	1.83	0.01	1.86 ± 0.07
$13 \leftarrow 12$	14.35	0.10	14.49 ± 0.14	1.83	0.01	1.83 ± 0.06
$14 \leftarrow 13$	14.07	0.10	13.99 ± 0.14	1.81	0.01	1.83 ± 0.06
$15 \leftarrow 14$	13.52	0.09	13.04 ± 0.13	1.89	0.01	1.80 ± 0.06
$16 \leftarrow 15$	11.78	0.09	11.77 ± 0.12	1.80	0.01	1.77 ± 0.06
$17 \leftarrow 16$	10.11	0.08	10.31 ± 0.10	1.72	0.01	1.74 ± 0.06
$18 \leftarrow 17$	8.32	0.08	8.761 ± 0.09	1.61	0.01	1.71 ± 0.06
$19 \leftarrow 18$	7.28	0.07	7.239 ± 0.07	1.66	0.02	1.68 ± 0.06
$20 \leftarrow 19$	5.51	0.07	5.82 ± 0.05	1.54	0.02	1.65 ± 0.06
$21 \leftarrow 20$	4.30	0.07	4.556 ± 0.05	1.40	0.03	1.62 ± 0.06
$22 \leftarrow 21$	2.87	0.06	3.476 ± 0.03	1.40	0.04	1.59 ± 0.06

W. Aenchbacher, M. Naftaly, and R. Dudley, “Line strengths and self-broadening of pure rotational lines of carbon monoxide measured by terahertz time-domain spectroscopy,” Applied Optics 43/13, pp. 2490, 2010.

N_2O Tabulated Results - Intensities

J'←J''	Line intensities (cm^{-1}/molecule.cm^{-2}) x 10^{-22}			J'←J''	Line intensities (cm^{-1}/molecule.cm^{-2}) x 10^{-22}		
	Measured		HITRAN (error not reported)		Measured		HITRAN (error not reported)
	value	error			value	error	
10←9	0.54	0.08	0.570	32←31	2.84	0.18	2.85
11←10	0.64	0.08	0.727	33←32	2.67	0.11	2.73
12←11	0.93	0.15	0.901	34←33	2.62	0.13	2.61
13←12	0.90	0.08	1.09	35←34	2.62	0.16	2.47
14←13	1.28	0.10	1.29	36←35	2.34	0.11	2.33
15←14	1.52	0.08	1.49	37←36	2.19	0.11	2.18
16←15	1.54	0.11	1.70	38←37	2.15	0.11	2.03
17←16	1.79	0.10	1.91	39←38	1.91	0.11	1.87
18←17	2.06	0.12	2.11	40←39	1.74	0.11	1.72
19←18	2.13	0.13	2.30	41←40	1.63	0.08	1.57
20←19	2.3	0.08	2.48	42←41	1.57	0.09	1.43
21←20	2.65	0.17	2.64	43←42	1.36	0.08	1.29
22←21	2.63	0.12	2.78	44←43	1.25	0.08	1.16
23←22	2.78	0.15	2.90	45←44	1.32	0.07	1.03
24←23	2.94	0.15	2.99	46←45	1.01	0.08	0.916
25←24	2.96	0.20	3.06	47←46	0.92	0.08	0.809
26←25	3.04	0.14	3.10	48←47	0.93	0.08	0.710
27←26	3.13	0.12	3.12	49←48	0.74	0.08	0.620
28←27	3.15	0.21	3.11	50←49	0.58	0.08	0.539
29←28	3.03	0.13	3.07	51←50	0.58	0.08	0.466
30←29	2.98	0.13	3.02	52←51	0.64	0.08	0.400
31←30	3.04	0.17	2.94	53←52	0.39	0.08	0.342

N_2O Tabulated Results – Self-Broadening

J'←J''	Self-broadening (GHz/atm)			J'←J''	Self-broadening (GHz/atm)		
	Measured		HITRAN		Measured		HITRAN
	value	error	2%≤ error ≤5%		value	error	2%≤ error ≤5%
10←9	3.1	0.3	3.24	32←31	2.7	0.1	2.61
11←10	2.7	0.6	3.21	33←32	2.5	0.1	2.61
12←11	3	0.4	3.18	34←33	2.6	0.1	2.58
13←12	2.5	0.5	3.12	35←34	2.7	0.1	2.58
14←13	3.1	0.2	3.09	36←35	2.5	0.1	2.55
15←14	2.8	0.2	3.06	37←36	2.6	0.1	2.55
16←15	2.8	0.2	3.03	38←37	2.6	0.1	2.52
17←16	2.8	0.2	2.30	39←38	2.8	0.1	2.52
18←17	3	0.2	2.97	40←39	2.5	0.1	2.49
19←18	2.8	0.2	2.94	41←40	2.6	0.1	2.49
20←19	2.6	0.1	2.91	42←41	2.6	0.1	2.49
21←20	2.9	0.2	2.88	43←42	2.6	0.1	2.46
22←21	2.6	0.1	2.85	44←43	2.6	0.3	2.46
23←22	2.8	0.1	2.82	45←44	3.1	0.3	2.43
24←23	2.8	0.2	2.79	46←45	2.6	0.4	2.43
25←24	2.8	0.1	2.78	47←46	2.8	0.5	2.43
26←25	2.7	0.1	2.76	48←47	3.4	0.3	2.40
27←26	2.7	0.1	2.73	49←48	2.5	0.2	2.40
28←27	2.8	0.1	2.70	50←49	2.7	0.4	2.40
29←28	2.6	0.1	2.67	51←50	2.7	0.5	2.37
30←29	2.7	0.1	2.67	52←51	3.4	1.1	2.37
31←30	2.8	0.1	2.64	53←52	2.3	0.4	2.37

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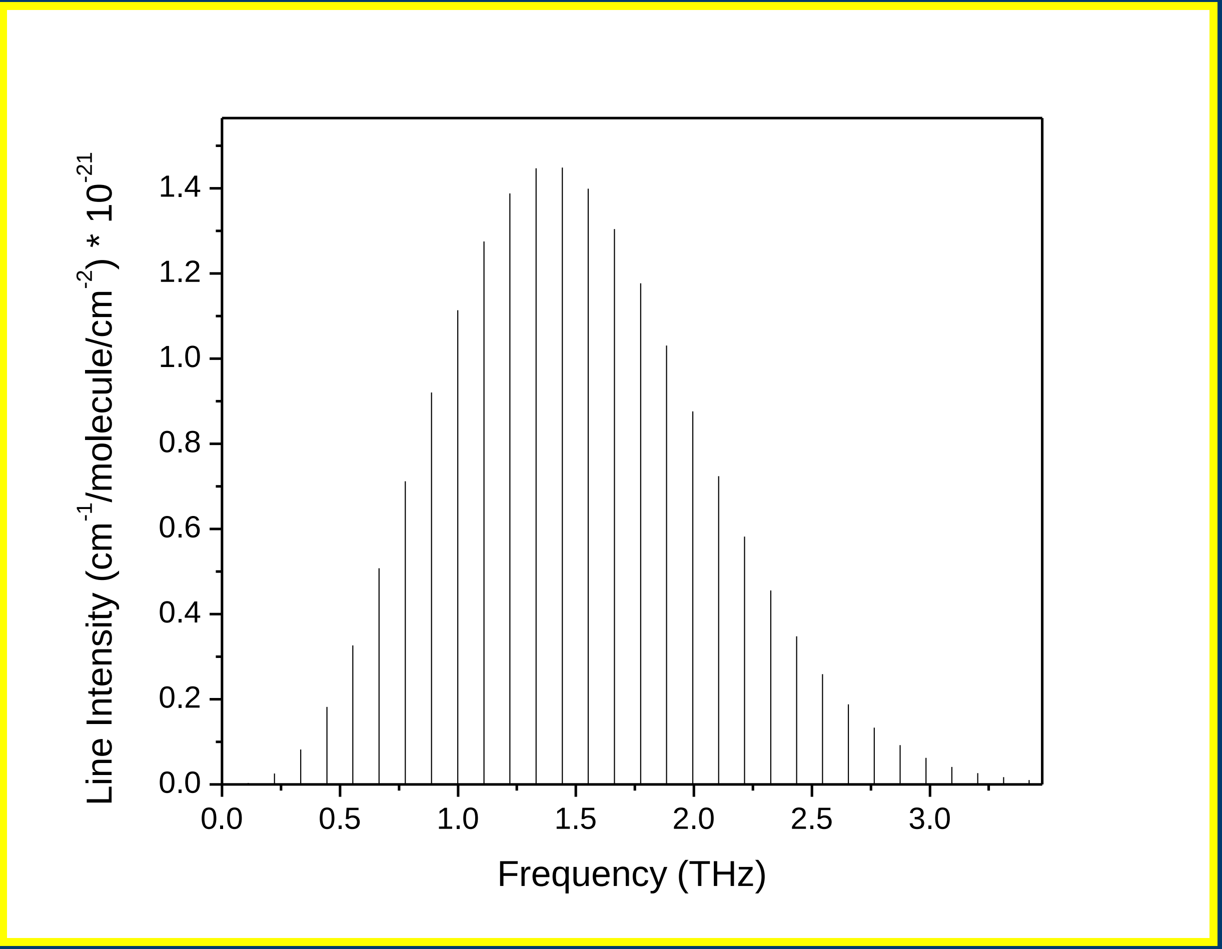
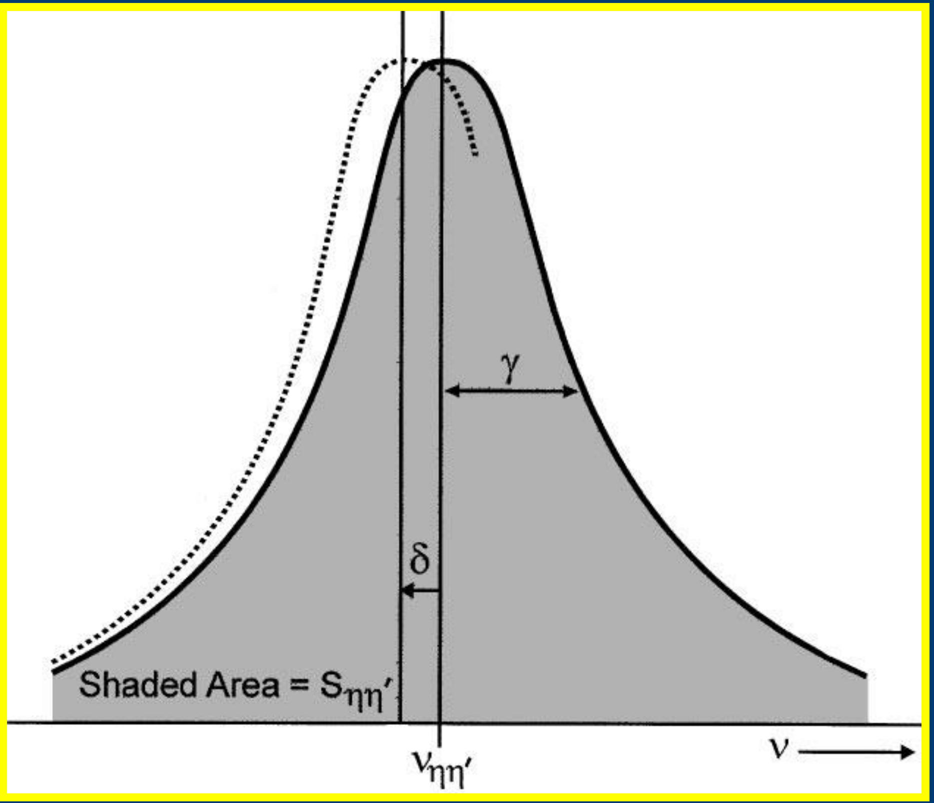
Carbon Monoxide



$$\upsilon_{J \to J+1} = 2B(J+1)$$

Line Parameters



L.S. Rothman, et al: The HITRAN molecular spectroscopic database and HAWKS (HITRAN atmospheric workstation): 1996 Edition, *J. Quant. Spectrosc. Radiat. Transfer Vol.* ***60/5****, 1999, pp 665-710.*

$$S = \int_{-\infty}^{\infty} \sigma(\upsilon)\, d\upsilon$$

where

$$\sigma(\upsilon) = \frac{\alpha(\upsilon)}{N}$$

Measuring Line Parameters

Assume each line is a Lorentzian:

$$\alpha_{J'}(\upsilon) = \frac{2A}{\pi} \frac{\Delta\upsilon}{(\upsilon - \upsilon_0)^2 + (\Delta\upsilon)^2}$$

and assuming an ideal gas:

$$S = \int_{-\infty}^{\infty} \sigma(\upsilon) d\upsilon = \frac{ktA}{P}$$

$$A(P) = \frac{SP}{kT}$$

obtain *A*(*P*) by Lorentzian fits at various pressures