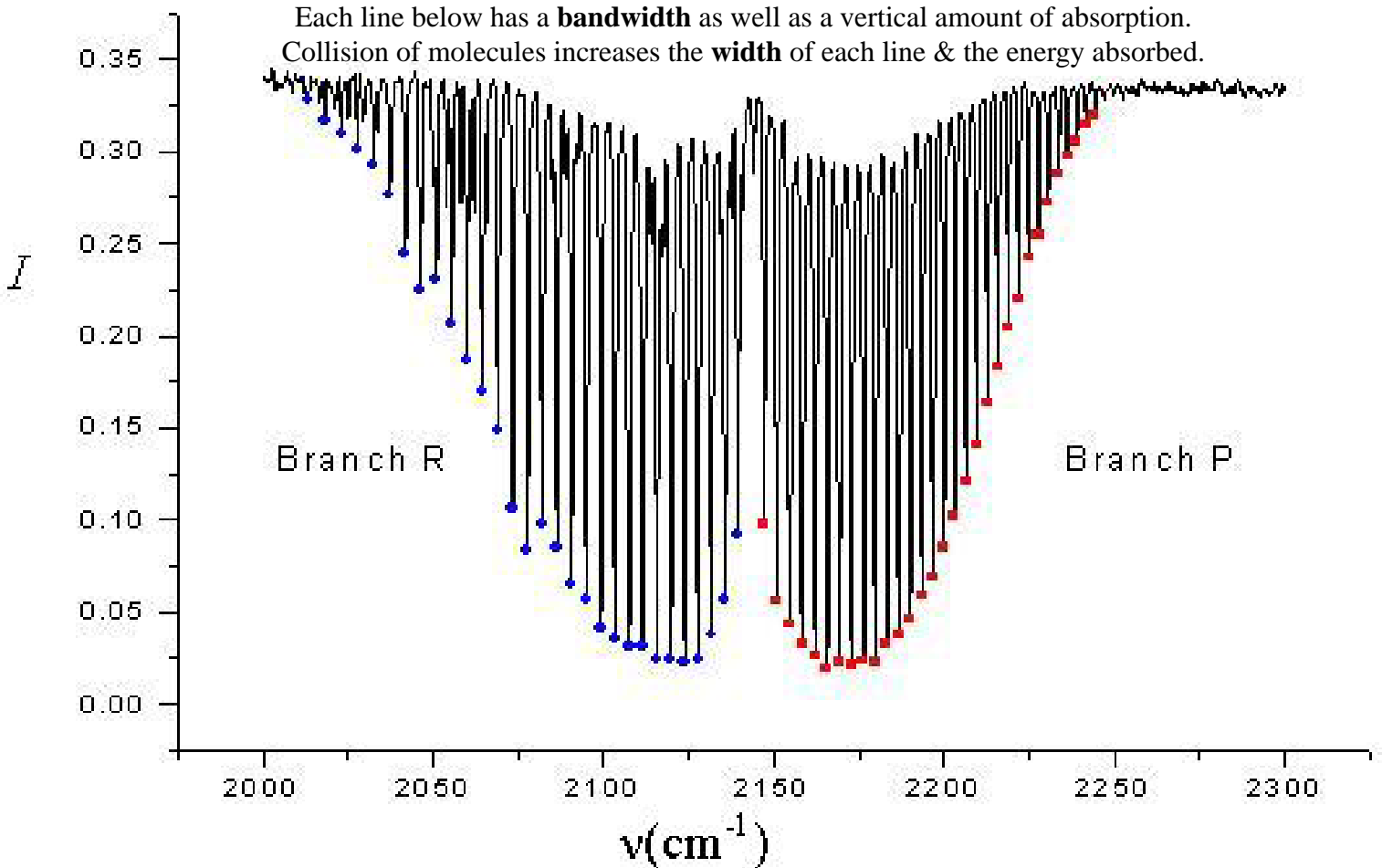


Mixtures of gas compounds may result in the broadening of the absorption lines for each compound. This is similar to increased atmospheric pressure effects or Gas Law effects (App note A12).

In the field of Infrared Spectroscopy, the phenomenon of pressure broadening is well know and documented (see attached references on page 4). The mechanism of pressure broadening includes **natural broadening**, **collisional broadening**, and **doppler broadening**. Of these three, **collisional broadening** has the greatest effect on the width and shape of the spectroscopic transitions. See **definitions** of Pressure or Collisional Broadening & Gas Law on page 2.

Carbon Monoxide (CO) absorption lines



Although **IR** absorption spectral responses are often shown as smooth curve responses (as is shown on page 2 with **CO₂**) they are more accurately shown as individual narrow frequency lines of absorption as shown in the plot of carbon monoxide above. The relatively narrow absorption lines created by the **CO** molecules are **broadened** by the **collisions** with **CO₂** molecules. This may increase the apparent interference of **CO₂** in the **CO** channel. The vertical length or intensity of the absorption depends upon the number of gas molecules in the optical path between the **IR** source and the **IR** detector/band pass filter. The Gas Laws affect the density and hence the number of molecules (see page 2). The impact is greater with heavy molecules. It increases the bandwidth of each line and hence the amount of energy absorbed by each line. See test data on page 3 & references on page 4.

Gas calibration with a **mixture** of **compounds** that will be measured will help to minimize this effect on accuracy. When we attempt to measure a gas compound using **NDIR** there is a **background compound** like air with 71% nitrogen or pure nitrogen (**N₂**) with a **molecular weight** of **28**. If you are trying to measure **CO** and you have a background of nitrogen the collision effect of the **N₂** molecules gives a baseline effect on the absorption lines of **CO**. If the background gas is **CO₂** with a molecular weight of **44** the molecular collisions will have more impact & a more significant effect on the absorption line broadening.

Gas Law definitions:

Boyle's Law: The proportionality between the pressure and volume of a gas may be expressed as follows:

V is proportional to 1/P or using a proportionality constant $V = k/P$ or $PV = k$

For a given sample of gas at constant temperature the product of the pressure of the gas and its volume will always be the same value

Charles's Law: At constant pressure, the volume of a gas is directly proportional to its absolute, or Kelvin temperature

$$V = mT$$

Gay-Lussac's Law: At constant volume, the pressure of a gas is directly proportional to its absolute, or Kelvin

$$\text{temperature. } P_1/T_1 = P_2/T_2 = P_3/T_3 = P_n/T_n = k$$

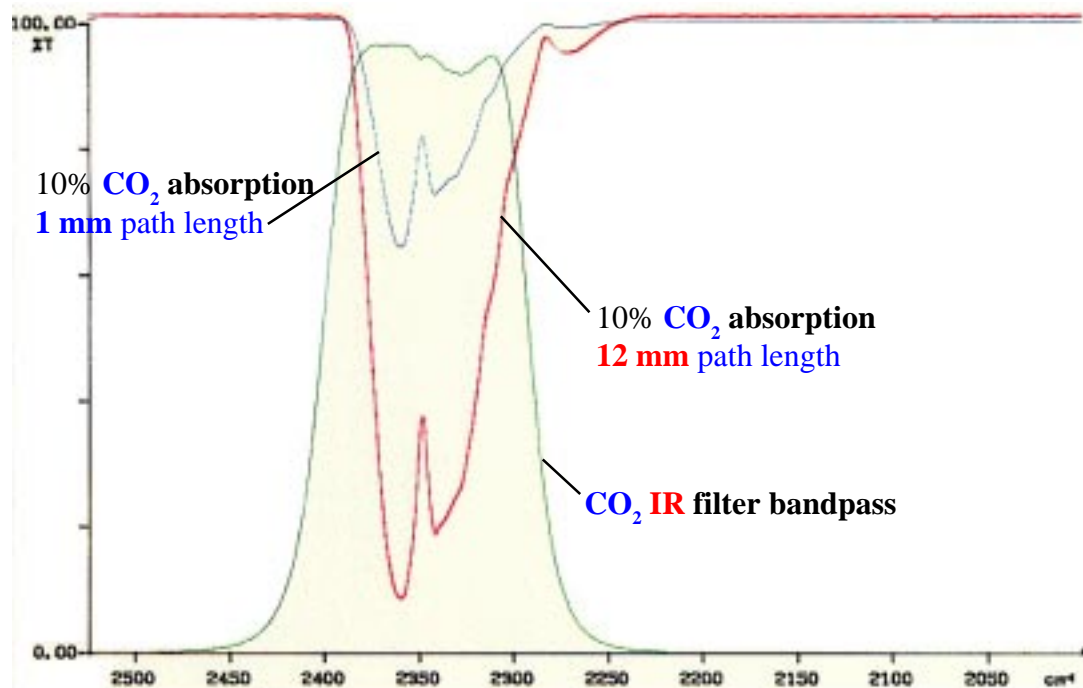
Combined Law Equation: $P_1 V_1 / T_1 = P_2 V_2 / T_2$

This equation shows there is a linear relationship when changes in absolute pressure, volume, or absolute temperature occur. Any change in either one of the three will affect either or both of the remaining ones.

Gas Density within a gas cell: In an **NDIR** gas cell the volume is held constant by the volume of the cell. The number of molecules between the **IR** source of energy and the **IR** band pass filter / **IR** detector (**path length**) is then determined by the absolute temperature and absolute pressure that effects the gas density (how close the molecules are to each other). See Application Note A12 for the quantified effects of temperature & pressure on **gas density**.

Effect on Spectral line shape & width by perturbing gases: In addition to the gas density changes that result in more or less gas molecules of interest in the path between the **IR** source & detector, the type of background gas molecules also has an affect on the amount **IR** energy absorbed. The **CO₂** absorption spectra shown below is a smooth approximation of the many individual narrow band absorption lines. The vertical depth of the absorption (inverse of the % transmission shown for the **IR** band pass filter) depends upon the **path length** and the gas density. The **width** of those **individual absorption lines** is affected by collisions with background gas molecules. Collisions with heavy background molecules cause the lines to get wider and more energy is absorbed.

% Transmission for filter



Wave number is the reciprocal of the wavelength in centimeters (the center wavelength is about 4.24 μM)

See **Application Note A12** for Gas Law effects of pressure and temperature changes from the atmospheric pressure & temperature at gas calibration time. See **Application Note A71** for **NDIR** sensor Theory of Operation.

Table 1 shows the response of an **NDIR CO** sensor for 0 to 20% **CO** by volume with nitrogen as a background gas and then a mixture of nitrogen and **20% carbon dioxide** flow blended in as a background gas. At 0.0% **CO** there would be 20% **CO₂**, at 5% **CO** there would be 15% **CO₂**, at 10% **CO** there would be 10% **CO₂**, at 15% **CO** there would be 5% **CO₂**, and at 20% **CO** there would be 0% **CO₂** as the chart shows. The 0-1V output response to **CO** of the sensor is increased by the collision of **CO₂** molecules with the **CO** molecules. **Graph 1** shows the amount of increased % **CO** due to these molecular collisions.

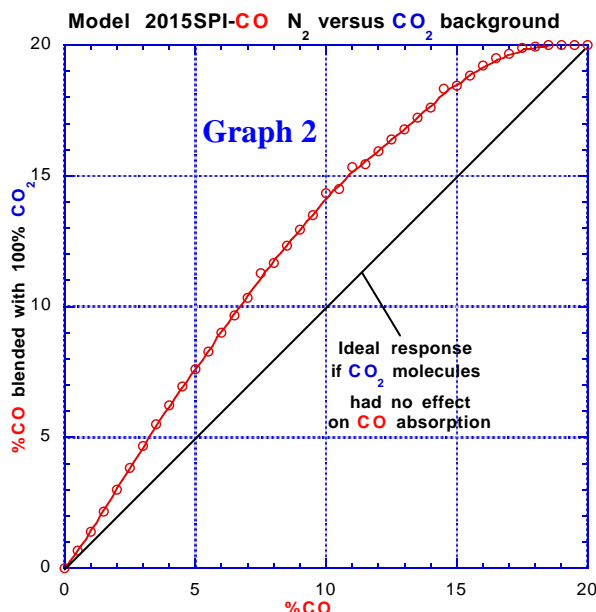
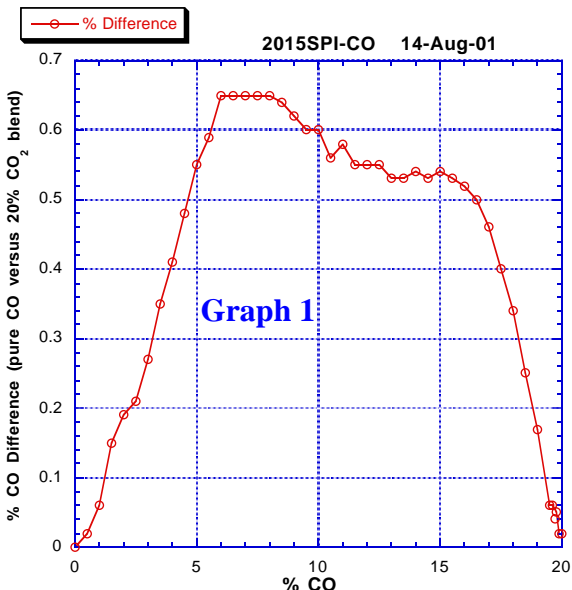
Table 2 shows the 0-1V response of an **NDIR CO** sensor to 0 to 20% **CO** by volume with nitrogen as a background gas. Then the same sensors response to a graduated mixture of 20% **CO** and **100% carbon dioxide** as a background gas. **Graph 2** is a plot of the 0 to 20% **CO** with nitrogen versus 100% **CO₂** background. We got nearly an identical response when we used a background of **100% propane (C₃H₈)**. Propane has no absorption spectra in this filter's band pass and we were careful to use additional out of band blocking teflon filters and an additional **CO** IR filter.

Table 1

%CO	Balance N2		Balance 20% CO ₂ & N ₂		Balance 20% CO ₂		Difference %CO
	0-1V	%CO ₂	0-1V	0-1V dif	%CO	%CO	
0.0	0.003	20.00	0.003	0.000	0.00	0.00	0.00
0.5	0.091	19.50	0.096	0.005	0.52	0.02	0.06
1.0	0.167	19.00	0.176	0.010	1.06	0.06	0.15
1.5	0.232	18.50	0.245	0.013	1.65	0.15	0.19
2.0	0.288	18.00	0.304	0.016	2.19	0.19	0.21
2.5	0.337	17.50	0.355	0.019	2.71	0.21	0.27
3.0	0.379	17.00	0.400	0.021	3.27	0.27	0.35
3.5	0.415	16.50	0.438	0.023	3.85	0.35	0.41
4.0	0.448	16.00	0.471	0.024	4.41	0.41	0.48
4.5	0.476	15.50	0.501	0.025	4.98	0.48	0.55
5.0	0.502	15.00	0.528	0.026	5.55	0.55	0.59
5.5	0.526	14.50	0.552	0.026	6.09	0.59	0.65
6.0	0.549	14.00	0.575	0.026	6.65	0.65	0.65
6.5	0.570	13.50	0.596	0.026	7.15	0.65	0.65
7.0	0.590	13.00	0.616	0.026	7.65	0.65	0.65
7.5	0.610	12.50	0.635	0.026	8.15	0.65	0.65
8.0	0.629	12.00	0.654	0.025	8.65	0.65	0.64
8.5	0.648	11.50	0.673	0.024	9.14	0.64	0.62
9.0	0.668	11.00	0.691	0.024	9.62	0.62	0.60
9.5	0.687	10.50	0.710	0.023	10.10	0.60	0.60
10.0	0.706	10.00	0.728	0.022	10.60	0.60	0.56
10.5	0.725	9.50	0.746	0.022	11.06	0.56	0.58
11.0	0.743	9.00	0.764	0.021	11.58	0.58	0.55
11.5	0.762	8.50	0.782	0.020	12.05	0.55	0.55
12.0	0.780	8.00	0.799	0.019	12.55	0.55	0.55
12.5	0.797	7.50	0.816	0.018	13.05	0.55	0.53
13.0	0.814	7.00	0.832	0.017	13.53	0.53	0.53
13.5	0.831	6.50	0.847	0.017	14.03	0.53	0.54
14.0	0.846	6.00	0.862	0.016	14.54	0.54	0.53
14.5	0.861	5.50	0.876	0.015	15.03	0.53	0.54
15.0	0.875	5.00	0.889	0.014	15.54	0.54	0.53
15.5	0.888	4.50	0.901	0.013	16.03	0.53	0.52
16.0	0.900	4.00	0.913	0.012	16.52	0.52	0.50
16.5	0.912	3.50	0.923	0.011	17.00	0.50	0.46
17.0	0.923	3.00	0.934	0.010	17.46	0.46	0.40
17.5	0.934	2.50	0.943	0.009	17.90	0.40	0.34
18.0	0.946	2.00	0.953	0.008	18.34	0.34	0.25
18.5	0.957	1.50	0.964	0.006	18.75	0.25	0.17
19.0	0.970	1.00	0.975	0.005	19.17	0.17	0.06
19.5	0.985	0.50	0.987	0.003	19.56	0.06	0.02
20.0	1.001	0.00	1.002	0.001	20.02	0.02	

Table 2

%CO	Balance N2		Balance 100% CO ₂ & N ₂		Balance 100% CO ₂		Difference %CO
	0-1V	%CO ₂	0-1V	0-1V dif	%CO	%CO	
0.0	0.000	100.0	0.000	0.000	0.00	0.00	0.00
0.5	0.103	97.5	0.129	0.026	0.65	0.15	0.39
1.0	0.183	95.0	0.233	0.050	1.39	0.39	0.65
1.5	0.248	92.5	0.315	0.067	2.15	0.65	0.99
2.0	0.301	90.0	0.382	0.081	2.99	0.99	1.33
2.5	0.345	87.5	0.437	0.092	3.83	1.33	1.67
3.0	0.383	85.0	0.484	0.101	4.67	1.67	1.98
3.5	0.417	82.5	0.525	0.108	5.48	1.98	2.20
4.0	0.447	80.0	0.560	0.113	6.20	2.20	2.42
4.5	0.475	77.5	0.593	0.118	6.92	2.42	2.63
5.0	0.501	75.0	0.623	0.097	7.63	2.63	2.80
5.5	0.526	72.5	0.651	0.125	8.30	2.80	3.00
6.0	0.550	70.0	0.678	0.128	9.00	3.00	3.18
6.5	0.574	67.5	0.703	0.129	9.68	3.18	3.36
7.0	0.596	65.0	0.727	0.131	10.36	3.36	3.80
7.5	0.618	62.5	0.749	0.131	11.30	3.80	3.69
8.0	0.639	60.0	0.770	0.131	11.69	3.69	3.83
8.5	0.659	57.5	0.790	0.131	12.33	3.83	3.93
9.0	0.678	55.0	0.809	0.131	12.93	3.93	4.00
9.5	0.697	52.5	0.826	0.129	13.50	4.00	4.03
10.0	0.714	50.0	0.843	0.129	14.33	4.33	4.33
10.5	0.732	47.5	0.858	0.126	14.53	4.03	4.33
11.0	0.748	45.0	0.872	0.124	15.33	4.33	3.97
11.5	0.764	42.5	0.885	0.121	15.47	3.97	3.93
12.0	0.780	40.0	0.898	0.118	15.93	3.93	3.87
12.5	0.796	37.5	0.910	0.114	16.37	3.87	3.77
13.0	0.811	35.0	0.921	0.110	16.77	3.77	3.70
13.5	0.826	32.5	0.932	0.106	17.20	3.70	3.60
14.0	0.842	30.0	0.942	0.100	17.60	3.60	3.83
14.5	0.857	27.5	0.952	0.095	18.33	3.83	3.47
15.0	0.871	25.0	0.962	0.091	18.47	3.47	3.35
15.5	0.886	22.5	0.971	0.085	18.85	3.35	3.20
16.0	0.900	20.0	0.979	0.079	19.20	3.20	3.00
16.5	0.914	17.5	0.986	0.072	19.50	3.00	2.65
17.0	0.927	15.0	0.991	0.064	19.65	2.65	2.37
17.5	0.939	12.5	0.996	0.057	19.87	2.37	1.97
18.0	0.951	10.0	0.999	0.048	19.97	1.97	2.00
18.5	0.963	7.5	1.000	0.037	20.00	1.50	2.00
19.0	0.974	5.0	1.001	0.027	20.00	1.00	0.50
19.5	0.986	2.5	1.001	0.015	20.00	0.50	0.00
20.0	1.000	0.0	1.000	0.000	20.00	0.00	



Conclusion:

The test data on page 3 clearly shows the upscale effect of pressure or collisional broadening on the **CO** response from the heavier **CO₂** molecule collisions with weight of **44** the instead of a nitrogen (**N₂**) background with a **molecular weight** of **28**. This increased absorption from the **broadening** of the absorption **line bandwidth** has similar effect as increasing the atmospheric pressure (increases gas density) which **lengthens** the absorption lines due to a larger number of molecules in the optical path. See Application Note A12 for more detail about the Gas Law effects.

If you **gas calibrate** with the same **mixture** of **compounds** that you will usually be measuring, you can minimize any adverse effect on accuracy. If you are measuring two gases like **CO** and **CO₂** with separate sensors you can cross compensate the **CO** response from the measured **CO₂** value based on the interference measurement. In many cases, the concentration of the interfering compound is not large enough to significantly effect your accuracy.

REFERENCES: **Note:** The URL links to WEB sites may change in the future so you may have to do a web search:

<http://www.chem.vt.edu/chem-ed/ac-basic.html> - Good reference for basics of **IR absorption**.

Beer-Lambert Law: The Beer-Lambert law (also called the Beer-Lambert-Bouguer law or simply Beer's law) shows the relationship between absorbance and concentration of an absorber of electromagnetic radiation.

See **page 25** of this **pdf**:

<http://www.ime-conrad.com/OEM/CPTCO2/co2guide.pdf>

Cardiopulmonary Technologies, Inc.

OEM Compact CO₂ Waveform Analyzer

MEASUREMENT OF PRESSURE-BROADENING LINE WIDTHS OF NO (nitric oxide) FROM THE FITTING OF LMR SPECTRA WITH CORRECTIONS OF INSTRUMENTAL BROADENING

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<http://www.worldscinet.com/journals/mplb/14/1411/S0217984900000537.html>

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State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan 430071, People's Republic of China

For absorption lines, the **distortion of spectral lines** by experimental spectrometers must be considered in measuring **linewidth** which has been investigated by many authors. While in the derivative spectrum, we managed to give the corrections of instrumental broadening and distortion to obtain accurate linewidths. We developed a universal fitting program which was explored together with the method of correction in the fundamental band spectra of LMR of NO. The uncorrected halfwidths were compared with the corrected values, which were obtained from the program. The results of comparison are very satisfactory and demonstrate their useful application to analyze experimental spectra.

Applied Physics B Lasers & Optics

<http://www.neo.no/applphysb98.pdf>

Horiba talks about a correction for line stretching due to other gas molecules being present.

http://global.horiba.com/semicon_e/ir-150/ir-150_08.htm

The reason for the IR-150's alternative **gas correction** Infrared property absorption band internal -C-H stretching vibration standard vibrations from 2960~2850 cm⁻¹ (3.38~3.51) appear as if they are near the absorption spectra.