

# Spectral Coincidences Between Emission Lines of the CO Laser and Absorption Lines of Nitrogen Oxides

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**Abstract**—Several spectral coincidences between carbon-monoxide laser emission lines and absorption lines of NO and N<sub>2</sub>O<sub>4</sub> have been observed, and absorption measurements have been taken. These data are presented and discussed along with similar spectral coincidence observations made previously using the helium-neon and iodine lasers. Other coincidences between CO-laser lines and NO<sub>2</sub> absorption lines are predicted from a study of recently available high-resolution-spectroscopy literature. Due to the narrow line widths of gas-laser lines, the coincidences reported here can be applied to the selective sensing of these constituents in the atmosphere.

WE REPORT a study of several spectral coincidences in the 5–6- $\mu$ -wavelength region between emission lines of the CO laser and absorption lines of NO and N<sub>2</sub>O<sub>4</sub>. Due to the fact that gas absorption linewidths are ordinarily very narrow compared with spacings between the lines, cases of overlapping gas-laser lines and molecular gas absorption lines are fortuitous and at the same time valuable in sensing the presence of these resonant constituents in the atmosphere. Cases of spectral coincidence have been reported previously. C. B. Moore has reported this phenomenon with the He-Ne 3.39- $\mu$  (3s<sub>2</sub> → 3p<sub>4</sub>) laser line (absorption by methane) [1]. P. Hanst has indicated similar coincidences with the CO<sub>2</sub>-laser lines at 9.5  $\mu$  (absorption by ozone) [2], and the iodine-laser lines at 4.862  $\mu$  (absorption by carbon monoxide) and 5.497  $\mu$  (absorption by NO) [2].

The liquid-nitrogen-cooled CO laser emits a multitude of lines at high-power levels in the 5–7- $\mu$  region [3], [4], and the room-temperature CO laser also emits several lines, most of them being at the longer wavelengths [5], [6]. Using published data on the nitric oxide fundamental absorption band [7] and the CO-laser emission-line data of C. K. N. Patel [3], and unpublished data of W. B. Lacina [6], we predicted several spectral coincidences. Some of these coincidences were observed using the CO laser, both at liquid-nitrogen temperature and at room temperature. In addition, certain room-temperature CO-laser lines in the 5.6–5.7- $\mu$  region were found to be strongly absorbed by N<sub>2</sub>O<sub>4</sub>.

The absorption data were taken by placing a 10-cm absorption cell with NaCl windows in the path of the

laser beam and passing the beam through a Jarrell-Ash one-meter Czerny-Turner spectrometer with a liquid-nitrogen-cooled InSb detector at the exit slit. Data were taken both for pure gases and for the gases in atmospheric-pressure backgrounds, in order to observe the effects of broadening and shifts of the absorption lines due to high pressures of foreign gases. The pressure-broadened linewidths at one atmosphere are quite large (about 0.1–0.2 cm<sup>-1</sup> [8], [9]). Since NO is oxidized by air, studies of foreign-gas broadening of the NO lines were made with high-purity nitrogen as a background gas. The N<sub>2</sub>O<sub>4</sub> absorption was then studied using air as a background gas.

In gaseous form, NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> exist together, their relative proportions depending on the total pressure and the temperature. At typical atmospheric concentrations, the predominant component is NO<sub>2</sub> and therefore absorption data for N<sub>2</sub>O<sub>4</sub> are probably not particularly relevant in the detection of atmospheric pollutants. However, they may be important in the study of reaction rates and high-resolution spectroscopy. At a total pressure of 50 torr, the ratio of NO<sub>2</sub>:N<sub>2</sub>O<sub>4</sub> is about 7:3 at room temperature, and it increases with increasing temperature. The observed N<sub>2</sub>O<sub>4</sub> absorption of the CO-laser lines disappears as the absorption cell is heated to 140°C, verifying that this absorption is due entirely to N<sub>2</sub>O<sub>4</sub> and not NO<sub>2</sub>.

Measurements of the absorption of the 3.3923- $\mu$  He-Ne laser line have been reported previously in a different context [1], [10]. The pressure broadening of this particular methane absorption line [ $\nu_3$  band, P(7)] by various foreign gases has also been studied, using Zeeman-tuned multimode lasers [11], [12]. We have studied this methane absorption line using a short He-Ne laser that could be operated in single TEM<sub>00q</sub> mode fashion at 3.3923  $\mu$  while being tuned over a region of  $\pm 150$  MHz from its line center [13].

Table I lists the data obtained using the CO laser, along with corresponding spectral coincidence data using the helium-neon and iodine lasers. All three of the absorbing gases listed play an important part in atmospheric photochemistry and the production of photochemical smog [14]. Several absorption measurements were made using pressures of pure NO in the 10–100-torr range. Results at two pressures, 20 and 50 torr, are shown. Since the Doppler width of the NO absorption line at room temperature is about 125 MHz (full width at half-maximum intensity), and the pressure broadening is of the order of 10 MHz/torr, the absorption lines for these pressures are partially

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TABLE I  
SPECTRAL COINCIDENCES BETWEEN LASER LINES AND MOLECULAR ABSORBERS

Gas	Identification	Absorption Coefficient, $\alpha$ (cm <sup>-1</sup> )			$\nu$ (cm <sup>-1</sup> )	Laser	Line of Laser	$\lambda$ vacuum	$\nu$ (cm <sup>-1</sup> )
		20 torr	50 torr	50 torr plus 700 torr N <sub>2</sub>					
NO	fundamental band, $R(18\frac{1}{2})$ , $\Omega = 3/2$	0.05	0.29	0.14	1935.53	CO (cooled)	7-6 band, $P(13)$	5.1666	1935.48
NO	fundamental band, $R(15\frac{1}{2})$ , $\Omega = 3/2$	0.05	0.20	0.20	1927.31	CO (cooled)	7-6 band, $P(15)$	5.1886	1927.28
NO	fundamental band, $R(3/2)$ , $\Omega = 1/2, 3/2$	0.065	0.14	0.28	1884.35	CO (cooled)	9-8 band, $P(13)$	5.3069	1884.37
NO	fundamental band, $P(9\frac{1}{2})$ , $\Omega = 1/2$	0.005	0.013	0.12	1842.98	CO	10-9 band, $P(17)$ or 9-8 band, $P(23)$	5.4265	1842.82
NO	fundamental band, $P(24\frac{1}{2})$ , $\Omega = 1/2$	0.006	0.016	0.025	1784.40	CO	12-11 band, $P(19)$	5.6043	1784.33
N <sub>2</sub> O <sub>4</sub>	$\nu_5$ or $\nu_9$ band††				0.12	CO	12-11 band, $P(18)$	5.5916	1788.40
N <sub>2</sub> O <sub>4</sub>	$\nu_5$ or $\nu_9$ band††				0.13	CO	12-11 band, $P(19)$	5.6043	1784.33
N <sub>2</sub> O <sub>4</sub>	$\nu_5$ or $\nu_9$ band††				>0.15†	CO	13-12 band, $P(17)$	5.6582	1767.36
N <sub>2</sub> O <sub>4</sub>	$\nu_5$ or $\nu_9$ band††				>0.10†	CO	13-12 band, $P(18)$	5.6710	1763.36
N <sub>2</sub> O <sub>4</sub>	$\nu_5$ or $\nu_9$ band††				>0.10†	CO	14-13 band, $P(14)$	5.7011	1754.06
NO	fundamental band, $P(15\frac{1}{2})$ ; $\Omega = 3/2$				1818.74	Iodine	$(^3P_2)5d[4]_{9/2}$ $\rightarrow(^3P_2)6p[3]_{7/2}$	5.4986	1818.62
CH <sub>4</sub>	$\nu_3$ band, $P(7)$		0.12 torr <sup>-1</sup> cm <sup>-1</sup> **		2947.91	He-Ne	$3s_2 \rightarrow 3p_4$	3.3923	2947.905

\* Probable identification of P. Hanst's observation [2].

\*\* At center of Doppler-broadened absorption line.

† The uncertainty in these data is caused by a weak relatively unstable laser output at this wavelength.

†† The rotational line spacing in this vibration-rotation band [ $\lesssim 0.5$  cm<sup>-1</sup>] is too small for us to make precise identifications of the absorption lines.

pressure broadened. (The pressure-broadening coefficient for the methane line previously mentioned has been reported to be 16 MHz/torr [15].)

For low pressures of an absorbing gas (not greater than one atmosphere), the lineshape near line center should take the form

$$\alpha_\nu = \alpha_0 \frac{a}{\pi} \int_{-\infty}^{\infty} \frac{\exp(-y^2) dy}{a^2 + (\omega - y)^2} \quad (1a)$$

or

$$\alpha_\nu/\alpha_0 = \text{Re } w^*(\omega + ia) \quad (1b)$$

where  $y$  and  $\omega$  are the frequency displacements from line center  $\nu_0$ , and  $a$  is the sum of the natural and pressure-broadening linewidths, all normalized by the Doppler linewidth [16]; and  $w(\omega + ia)$  is the error function for complex arguments [17]. The quantity  $\alpha_0$  depends on the line strength and the number of absorbing molecules [16]. If one measures the absorption at line center for this case, at pressures less than a torr, one can obtain an absorption coefficient that is linearly proportional to pressure.

Our data for NO absorption are not at the centers of the lines, since the spectral coincidences are not exact, and we had no means of tuning the CO-laser lines in order to find the line centers. In addition, at pressures ranging from 10 to 100 torr, where we took our data, shifts and broadenings of absorption lines due to collision effects

can appear. Consequently we present our data at representative pressures and refrain from drawing any quantitative conclusions concerning the values of the absorption coefficients at the centers of the lines. On the other hand, the methane absorption measurements were taken at much lower pressures, and we had the ability to tune the laser line to the peak of the absorption line, which entailed a frequency shift of about 125 MHz. Thus the absorption coefficient for the methane line presented in Table I is the result of data taken at pressures below 1 torr and at the center of the predominantly Doppler-broadened absorption line.

The  $\nu_3$  absorption band of NO<sub>2</sub> ranges from 1550 to 1650 cm<sup>-1</sup>, which falls in the wavelength region covered by the Q-switched liquid-nitrogen cooled CO laser. The recent accurate measurements of the emission lines of this laser by Mantz *et al.* [4] have made possible the prediction of several coincidences between these laser lines and the absorption lines of NO<sub>2</sub> [18]. Coincidences between CO-laser lines and NO<sub>2</sub> absorption peaks that are within  $\pm 0.01$  cm<sup>-1</sup> are listed in Table II. A few of these coincidences might be close enough so that the laser lines could be tuned to exact coincidence with the NO<sub>2</sub> absorption peaks using a piezoelectric translator (PZT) on one mirror.

With atmospheric-pressure broadening, a coincidence within about  $\pm 0.1$  cm<sup>-1</sup> would ensure absorption of the

TABLE II  
COINCIDENCES BETWEEN MEASURED CO LASER LINES AND  
ABSORPTION LINES OF THE  $\nu_3$  BAND OF  $\text{NO}_2$   
TO WITHIN  $\pm 0.01 \text{ cm}^{-1}$

Line of Laser	$\nu(\text{cm}^{-1})$
18-17 band, P(13)	1658.23
19-18 band, P(8)	1651.30
20-19 band, P(6)	1633.31
20-19 band, P(10)	1619.57
22-21 band, P(10)	1570.37
23-22 band, P(8)	1552.62
23-22 band, P(11)	1542.46

CO-laser line by  $\text{NO}_2$ . Since the spacing of the  $\text{NO}_2$  absorption lines throughout most of this band is  $0.2 \text{ cm}^{-1}$  or less, almost every laser line in this wavelength region would be absorbed to some extent by  $\text{NO}_2$  in an atmospheric background. The detection of  $\text{NO}_2$  in the atmosphere is further complicated by strong water-vapor absorption in this spectral region [18].

It would be profitable to conduct more extensive studies of these absorption lines with the use of an external frequency shifter. Since the Doppler-gain profiles of the CO-laser lines have widths of about 100-200 MHz, depending on the mode of operation, the tuning range of a PZT mirror scan is limited. The CO laser used in these measurements did not have a PZT mirror scanner, thus the accuracy of our absorption data for the 20-torr column of Table I is limited due to frequency drifts of the laser lines about their respective line centers. At higher gas pressures, the absorption linewidths are much larger than the Doppler widths of the laser-line gain profiles, making the absorption data less sensitive to drifts caused by slight changes in the laser-cavity length.

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