AN EXPERIMENTAL STUDY ON ABSORPTION PROPERTIES OF NO, NO₂, NH₃, CO₂ AND H₂O BY USING LINE-TUNABLE CO LASER

Wang Gengchen (王庚辰) and *Kong Qinxin* (孔琴心)

Institute of Atmospheric Physics, Academia Sinica, Beijing

ABSTRACT

Measurements of absorption properties of some gases in the atmosphere were made by using CO line-tunable laser. Experimental equipment and method are briefly described. Absorption coefficients of NO, NO₂, NH₃, CO₂ and H₂O at some definite laser wavelengths are given, and variations of absorption properties with both partial and total pressures are discussed.

I. INTRODUCTION

A new way for the remote measurement of gases in the atmosphere was opened up by using laser, especialy by using line-tunable laser. Infrared laser takes an important place in this circle, because the majority of atmospheric compositions and pollutant gases have their own characteristic wavelengths in infrared region. Nowadays environmental pollutants, which can be measured by laser, amount to about 40, and 90% these laser-measured pollutants are gases[1]. However, the real atmosphere is a mixed environment containing many kinds of gases, so that laser wavelengths, carrying imformation of measured matter, are always interfered by many gases in the atmosphere. Therefore, when a gas is to be measured by using line-tunanle laser, a measuring wavelength must be carefully selected and the interaction between the selected laser wavelength and the gas should be known very well. Measurements of absorption properties of NO, NO₂, NH₃, CO₂ and H₂O were made by using CO line-tunable laser in our laboratory. Experimental equipment and method are briefly described, and some results are given and discussed in this paper.

II. SINGLE LINE ABSORPTION

The single line absorption coefficient $k(\gamma)$ at frequency γ is described as[2]

$$k(\gamma) = sf(\gamma - \gamma_0), \tag{1}$$

where s is the integrated intensity of an absorption line, γ_0 is the central position of the line, and $f(\gamma - \gamma_0)$ is the line shape of the absorption line, which mainly depends on broadening mechanism in the atmosphere in the absence of strong external electro-magnetic field. Under low pressure where the Doppler broadening plays a dominant role (for example, in the atmosphere above 26 km for CO_2 4.3 μ band), the expression for $k(\gamma)$ is given by

$$k_D(\gamma) = (\ln 2/\pi)^{\frac{1}{2}} (s/\alpha_D) \exp\{(-\ln 2)[(\gamma - \gamma_0)/\alpha_D]^2\}, \tag{2}$$

where α_D is known as the Doppler half-width and is written as

$$\alpha_D = \gamma_0 [2\ln 2/(MC^2/RT)]^{\frac{1}{2}}, \tag{3}$$

where M is the mole of the gas, C is the light speed, R is the gas constant, T is temperature.

In lower part of the atmosphere where spectral lines of all atmospheric molecules are largely broadened identically, the line shape of absorption lines is mainly determined by Lorentz broadening and $k(\gamma)$ is written as

$$k_L(\gamma) = (\alpha_L s/\pi)/[(\gamma - \gamma_0)^2 + \alpha_L^2],\tag{4}$$

where α_L is the Lorentz half-width. For the absorption at line centre formulas (2) and (4) are rewritten as

$$k_D(\gamma = \gamma_0) = (\ln 2/\pi)^{\frac{1}{2}}(s/\alpha_D),\tag{5}$$

$$k_L(\gamma = \gamma_0) = s/\pi\alpha_L.\tag{6}$$

If we designate $\alpha_{L,0}$ and s_0 as the Lorentz half-width and the integrated intensity under the normal pressure and temperature, thus we have

$$\alpha_L = \alpha_{L,0}(p_e/p_0)\ (T_0/T)^n,\tag{7}$$

$$s = s_0(T_0/T)^b \exp\{(-E''/k)[(T_0 - T)/T_0 T]\},\tag{8}$$

where p_e is the equivalent pressure, E'' is the energy of the lower state, k is the Boltzmann constant, n and b are constants.

For practical application where both Doppler and Lorentz broadening should be considered, the Voigt line shape is applied and the expression for $k(\gamma)$ takes a form[3]

$$k_V(\gamma) = (k_0 a/\pi)\int_{-\infty}^{+\infty} \{\exp(-t^2)/[a^2 + (x - t)^2]\}dt,\tag{9}$$

where $\quad k_0 = (s/\alpha_D)(\ln 2/\pi)^{\frac{1}{2}}, \quad a = (\alpha_L/\alpha_D)(\ln 2)^{\frac{1}{2}}, \quad x = [(\gamma - \gamma_0)/\alpha_D](\ln 2)^{\frac{1}{2}}.$

III. EXPERIMENTAL EQUIPMENT AND METHOD

The experimental equipment consists of laser source, external optical system, sample absorption cell, detector, amplifier and recording system (Fig. 1). As radiation source, XZJ-1 type line-tunable CO laser consists of a laser tube, a grating tuning platform and a stabilized current source. Output laser wavelegths can be selected easily by adjusting a special handle. This laser can emit about 95 lines in spectral region 5.2—6.3 μ under room temperature. External optical system consists of beam splier BS, chopper C, plane mirrors M_1 and M_2, 6328Å He-Ne laser and optical diaphragms A_1, A_2, A_3 etc. Sample cell is a absorption cell with a physical length of 3 m and maximum optical length of 300 m. The cell is equipped with a system for measurements of vacuum, pressure and sample concentration. Laser beam from the source is partly reflected by the BS into the detector D_2 as a controling beam, the rest of the beam goes through BS into the absorption cell by the reflection of M_1 and M_2. Inside the cell laser beam travels to and fro several times and at last goes out of the cell and reaches detector D_1, that is the geometry of measuring beam. The He-Ne laser is used for guiding the infrared radiation.

Errors caused by the instability of the laser source and the variation of instrumental constants are eliminated by using ratio of controling and measuring beams in our measurement of transmittance $T(\gamma)$. The absorption coefficient $k(\gamma)$ in this case can be obtained easily from the measured $T(\gamma)$, i.e.

$$T(\gamma) = [I_1(\gamma)/I_2(\gamma)]/[I_1'(\gamma)/I_2'(\gamma)] = \exp[-k(\gamma)U \cdot L],\tag{10}$$

where $I_1(\gamma)$ and $I_1'(\gamma)$ are the radiation intensities of the controling beam at different times respectively, $I_2(\gamma)$ and $I_2'(\gamma)$ are that of the measuring beam before and after passing through the absorption cell containing sample, respectively, U is the sample concentration and L is the length of optical path. In
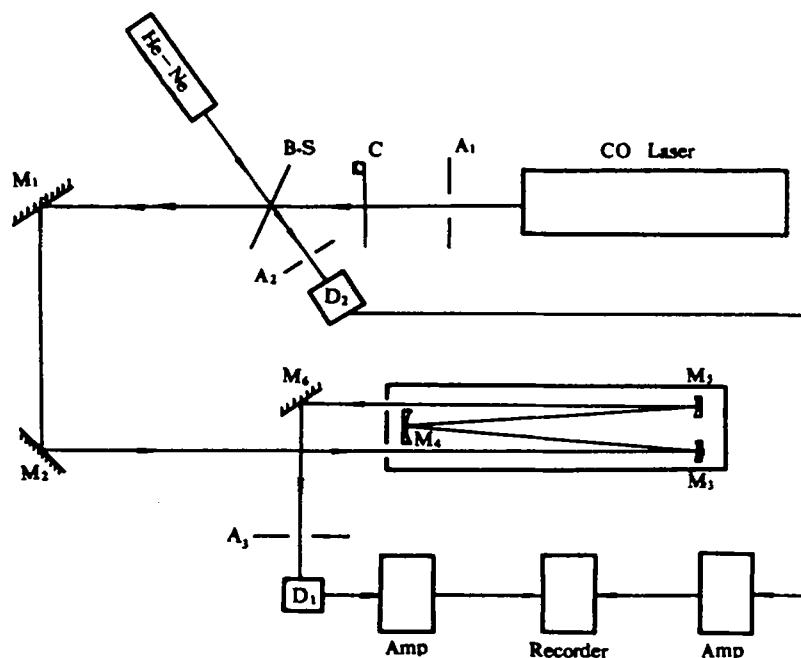
Fig. 1.   Diagram of experimental equipment .

our experiments the samples which contain 1% NO or NO_2 are specially made, while the samples of NH_3 or CO_2 are the pure gases without other constituents.

Spectral lines emitted by line-tunable CO laser are all in the region of 5.2—6.3 μ[4] having a large number of H_2O absorption lines. Therefore, all laser lines are influenced more or less by absorption lines of H_2O[5], that is the reason why the ultra-pure nitrogen was used as a broadening gas in our study. As space is limited here only some results for resonance absorption properties are given and discussed, this means that frequences between the selected line of laser and the absorption line of measured sample essentially coincide. In general, the difference between their central frequences is not larger than the halfwidth of the corresponding absorption line.

IV. THE ABSORPTION OF NO, NO_2, NH_3, CO_2 AND H_2O

1.   Absorption Coefficients

All selected wavelengths of CO laser v_{CO} and the corresponding wavelengths of sample resonance absorption lines v_R are listed in Tab.1. Resonance absorption coefficients k of NO, NO_2, NH_3, CO_2 and H_2O are also given in Table 1. These results provide not only useful data for studying single line absorption of these gases, but also a scientific basis for the remote sensing of the concentration of these gases in the atmosphere and for the evaluation of environmental quality. Water vapour absorption coefficients k_{H_2O} for all selected wavelengths of CO laser are also given in Tab.1 for selecting suitable laser wavelengths and for reasonable data processing in practical application. No doubt, owing to the interference effect, more attention must be paid to the influence of water vapour on the measurement result in practical application. Of course, this influence is different for different methods and technology applied in the measurement. For example, the detection sensitivity will be greatly decreased due to the

Table 1. Absorption Coefficients of NO, NO$_2$, NH$_3$, CO$_2$ and H$_2$O

ν_{CO} (cm^{-1})	ν_R (cm^{-1})	Gases	k (atm. cm^{-1})	k_{H_2O} (cm^2/g)
1829.592	1831.830	NO	1.309	362.400
1842.808	1842.980	NO	3.356	40.486
1863.655	1863.690	NO	1.159	8.714
1876.630	1875.880	NO	0.180	20.200
1605.265	1605.278	NO$_2$	41.056	22.029
1619.564	1619.570	NO$_2$	32.345	66.286
1633.313	1633.310	NO$_2$	74.756	76.114
1880.901	1881.000	CO$_2$	7×10^{-3}	2.286
1626.175	1626.175	NH$_3$	7.188	64.057
1656.260	1656.290	H$_2$O		129.42
1746.298	1746.280	H$_2$O		336.66
1788.397	1788.400	H$_2$O		54.54
1796.928	1796.910	H$_2$O		127.94
1876.630	1876.629	H$_2$O		20.20

absorption effect of water vapour if 1863.655 cm^{-1}, 1605.265 cm^{-1} and 1626.175 cm^{-1} laser lines are used for a long-path absorption measurement of NO, NO$_2$ and NH$_3$ respectively. An estimation indicates that equivalent contents of NO, NO$_2$ and NH$_3$ caused by the absorption effect of water vapour are 2.2, 0.2 and 3.1 · atm. cm, respectively, when 0.35 g/cm^2/km of water vapour content is suggested (that corresponds to the middle-latitude winter atmosphere). That means the detection sensitivity of long-path absorption method is low, and this method can only be used effectively for the measurement of a strong pollutant source. However, if the measurement method is improved (for example, a gas correlation technology is used), the influence of water vapour on the measurement result will be decreased greatly, and it will be possible to measure the background contents of the above-mentioned gases. Generally speaking, no matter which method and technology are used, in order to increase the detection sensitivity and decrease the error in concentration measurements over a given path by absorption method, such laser wavelengths should be selected that are more absorbed by measured gas and less interferred by other gases. The data in Table 1 show that it is effective to detect the concentration of atmospheric water vapour and NO$_2$ in the atmosphere by using CO laser, because some lines of CO laser are absorbed strongly by these gases. Detection of concentration of NH$_3$ and NO are also effective by using CO laser.

2. Variation of Absorption Properties

According to the single line absorption theory, in certain range of pressure and concentration, gas absorption at a given wavelength is directly proportional to partial pressure of the gas. Some examples for the variations of absorption of NO, NO$_2$, CO$_2$ and H$_2$O with their partial pressures are given in Fig. 2—5. Total pressure in all examples is 760 mm Hg. These figures show that within the range of our experiment the variations of absorption of these gases with their partial pressures can very well be described by simple linear relations.

In addition to the study of the variations of gas absorption with their partial pressures, the effects of total pressure on the gas absorption were also studied. Deep-going study of these

effects is the most important contants in molecular spectroscopy of atmospheric gases. It is important both for theory and for practical applications, because the total pressure varies in quite large range in the atmosphere. According to the single line absorption theory, under unsaturated absorption, pressure broadening weakens the absorption at the centre of a absorption line, but the problem is more complicated in the wings of the absorption line. Some variation curves of the absorption of NO, NO_2, NH_3 and H_2O with the variation of total pressure under a given partial pressure are given in Fig. 6—9 respectively. These Figures show clearly that although the all selected wavelengths of CO laser locate near the absorption line centres of corresponding absorption gases, variations of gas absorptions are very different. Fig.7 indicates that absorptions at 4 wavelengths of CO laser by NO increase with increasing total pressure. This characteristic of absorption variation is consistent with that for the wings of absorption line . That means that these laser lines either located exactly at the wings of NO absorption lines or there are some other strong NO absorption lines near the resonance absorption line (see later). Results in Fig.6, 8 and 9 are more complicated than that in Fig.7. As an example, the broadening effect of N_2 for H_2O resonance absorption is analysed below in detail.

Absorption curves for 5 lines of CO laser are given in Fig.9. Among them, the absorptions for two lines—1876.630 cm^{-1} and 1746.289 cm^{-1} —— vary as the absorption at line centre, that is, absorption increases with decreasing total pressure. For instance, absorption coefficients for these two lines at 200 mmHg total pressure are 3.5 and 1.5 times larger, respectively, than that at 760 mmHg total pressure. With increase of total pressure, the absorption lines are broadened gradually and absorptions for these two lines are weakened. Absorptions for the rest 3 lines vary mainly in consistent with that at absorption line wing, that is, absorption increases with increase of total pressure. Analysis indicated that the main cause producing the inconsistent of these absorption variations with that at line centre is the interference of the nearest H_2O absorption lines. Detailed analysis shows that H_2O absorption line at 1876.610 cm^{-1} is a strong isolated line, and that within its half-width, even within 1 cm^{-1} of each side of this line, there are no other H_2O absorption lines, whose intensities can be compared with that of the resonance line. Some weak H_2O absorption lines exsist near this resonance line, but their intensities are 10^4—10^5 times weaker than that of the resonance line . Further calculation shows that contribution of these nearest weak lines to the absorption at 1876.630 cm^{-1} is no more than 1%. Therefore, for the laser line at 1876.630 cm^{-1}, the absorption is caused mainly by the line of H_2O at 1876.610 cm^{-1}, that is why the absorption variation for this laser line follows the absorption rule at line centre. It is almost the same for the absorption variation at 1746.298 cm^{-1}, but here the interference of the nearest H_2O absorption lines is very obvious.

Characteristics of absorption variation for the rest 3 lines of CO laser are quite different from that for the above-mentioned 2 lines. In addition to the resonance H_2O absorption lines, there also exist some other strong H_2O absorption lines near these laser lines. For example, absorption for laser line at 1788.397 cm^{-1} is caused by many absorption lines of water vapour. Around the resonance H_2O absorption line at 1788.400 cm^{-1}, there exist many H_2O absorption lines, whose intensities are comparable with that of the resonance absorption line or only about 10 times less than that. No doubt, pressure broadening can enlarge the contribution of these lines to the absorption at 1788.397 cm^{-1} laser line. As a result, although this line of CO laser locates very close to H_2O resonance abosorption line, its absorption variation does not follow absorption rule of line centre. It must be noticed that when the broadening effect of single line is studied by using line-tunable laser, more attention should be paid to the overlapping of some absorption lines, precision of laser wavelengths and possible shift of relative position between

given laser wavelength and absorption line under a definite total pressure. For example, under a low pressure, the selected laser line locates initially outside the half-width of a given absorption line, but with the increase of total pressure the relative position between these two lines changes and the laser line seems to shift to the central part of the given absorption line. This shift is seen in Fig.6, showing a absorption variation of NO_2 for 1633.313 cm^{-1} laser line by pressure broadening.

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[5]   孔琴心, 张文, 王庚辰, 大气科学, 7 (1983), 102—107.
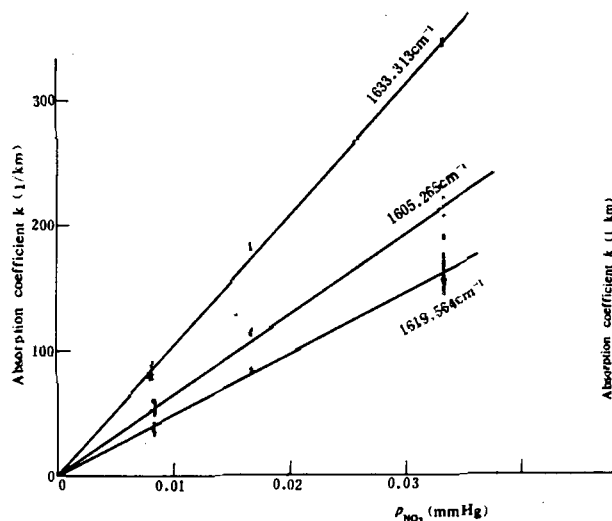
Fig. 2 .   Variation of NO_2 attenuation coefficient with
partial pressure ($p_t = 760$ mmHg).
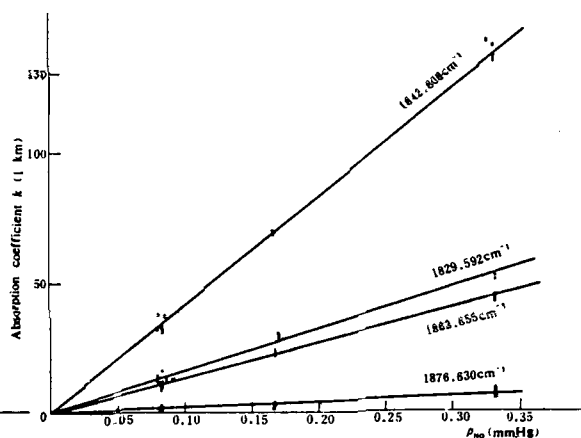
Fig. 3.   Variation of NO attenuation coefficient with
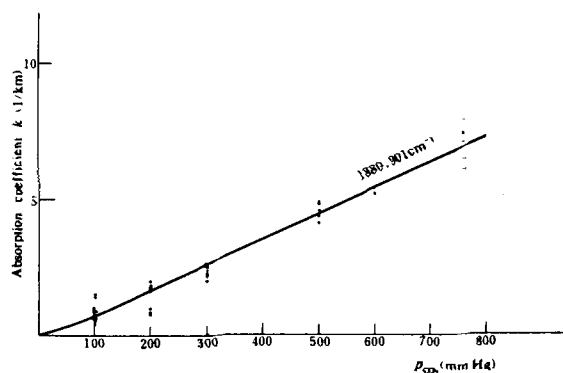partial pressure ($p_t = 760$ mmHg).

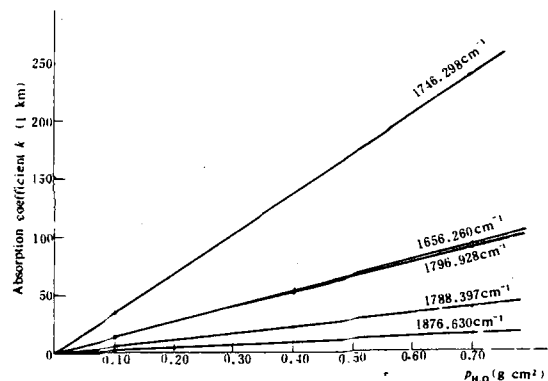Fig. 4.   Variation of CO_2 attenuation coefficient with
partial pressure.

Fig. 5.   Variation of H_2O attenuation coefficient with
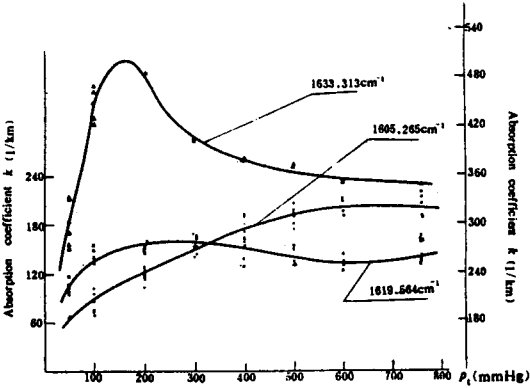partial pressure ($p_t = 760$ mmHg).

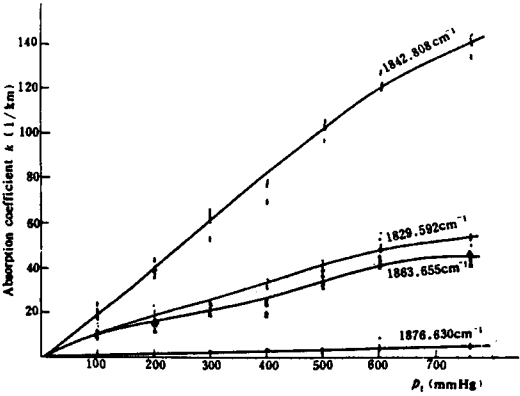**Fig. 6.** Pressure broadening by N_2 in NO_2 absorption ($p_{NO_2} = 3.33$mmHg).
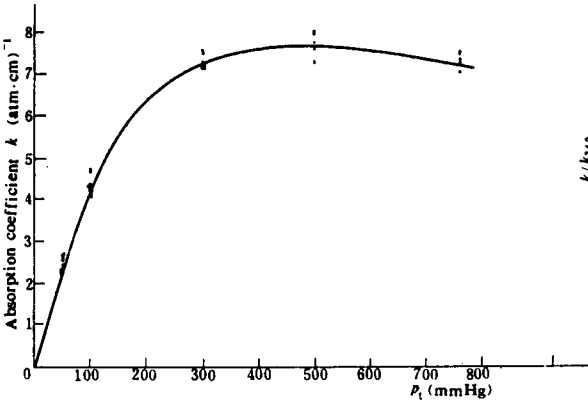
Fig. 7. Pressure broadening by N_2 in NO absorption.

Fig. 8. Variation of NH_3 absorption coefficient with total pressure ($p_{NH_3} = 2.4$ mmHg).
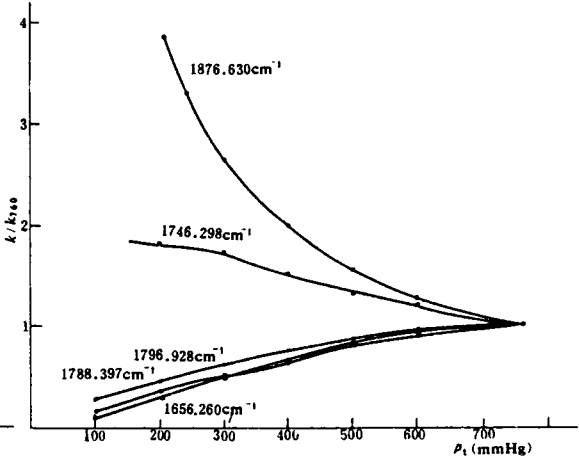
Fig. 9. Variation of CO laser line absorption by H_2O with pressure.