A STUDY ON NO AND NO₂ ABSORPTION PROPERTIES 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

The absorption properties of NO in 5.2 μm band and NO₂ in 6.2 μm band are measured for some definite wavelengths by using line-tunable CO laser and long-path absorption cell. The absorption coefficients for 49 CO laser wavelengths are given and variations of absorption withpartial and total pressures are analysed. Furthermore, the experimental errors and the interference of water vapour with the absorption at definite laser lines are also discussed.

I. INTRODUCTION

The laser, especially line-tunable laser, opens a new way to monitoring the atmospheric environment and has been effectively applied. The infrared laser is even more interesting because most trace gases in the atmosphere have their own characteristic wavelengths in the infrared region. At present, trace gases in the atmosphere, which can be measured by laser, amount to about 40 (Patel, 1978). The nitric oxides are an important pollutant produced in the processes o exhaust and combustion. Through oxidation in the atmosphere, NO becomes NO₂ whose poisonousness is about 5 times as great as that of NO. The poisonousness would be even greater if NO₂ takes part in the formation of chemical fog under the action of the solar radiation. In addition, NO and NO₂ are of importance for the photochemical cycle in the stratosphere. Therefore, they are an important object in atmospheric pollutant monitoring. When a given pollutant gas is going to be measured by infrared laser, the measuring wavelength, on the one hand, should be selected carefully to avoid an interference from other gases in the atmosphere and, on the other hand, an interaction between the measured gas and the selected laser lines should be known very well. Therefore, an experimental study on NO and NO₂ absorption properties by using CO line-tunable laser has been carried out. The present paper presents and discusses the theory of a single-line absorption, the experimental equipment and methods used, and some of the results obtained therefrom.

II. THEORY OF SINGLE-LINE ABSORPTION

A single line absorption coefficient $k(\nu)$ at frequency ν is written as

$$k(\nu) = Sf(\nu - \nu_0),\qquad\qquad (1)$$

where S is the integrated line intensity of transition spectral line, ν_0 the central position of the absorption line, $f(\nu - \nu_0)$ the profile factor of the absorption line, which mainly depends on the broadening mechanism in the atmosphere in the absence of external electro-

magnetic field.   In present work, absorption coefficients of NO and NO₂ are measured under the total pressure of 50 mmHg and more, so the Lorentz broadening is dominant.   Suppose that the self–broadening effect is not important (for NO and NO₂ the self–broadening co-efficient nealy equals 1) and S_0, α_0 and k are measured at the same temperature, then, for the Lorentz broadening, we have (Bair et al., 1977):

$$k_P(\nu) = \frac{S_0 P}{\alpha_0 \pi P_0} \frac{1}{b_0^2 \left[1 - \frac{\varepsilon}{\Delta \bar{\nu}}\left(\frac{P}{P_0}\right)\right]^2 + \left(\frac{P}{P_0}\right)^2} , \qquad (2)$$

where $b_0 = \frac{\Delta \bar{\nu}}{\alpha_0}$, S_0 and α_0 are the intensity and halfwidth of a single absorption line under

the standard conditions, respectively. $\Delta \bar{\nu}$ is the difference between the frequencies of the laser emission line and the corresponding NO$_x$ absorption line; ε stands for the drift of absorption line position with broadening process.   Suppose that $P = 1$ atm., then Eq. (2) can be simplified as

$$k_{P_0} = \frac{S_0}{\alpha_0 \pi} \frac{1}{b_0^2 \left[1 - \frac{\varepsilon}{\Delta \bar{\nu}}\right]^2 + 1} . \qquad (3)$$

A relationship between the absorption coefficient k_ν and the transmittance τ_ν is

$$\tau_\nu = \frac{I_\nu}{I_{\nu,0}} \exp(-k_\nu u), \qquad (4)$$

where $I_{\nu,0}$ and I_ν are the measured signal intensities before and after absorbing by samples, respectively; u is the sample concentration.

III. EXPERIMENTAL EQUIPMENT AND METHODS

The whole experimental equipment consists of the laser source, external optical system, sample absorption cell and detector–recording system (Fig. 1).   The XZJ-1 type CO line-tunable laser is used as a radiation source, which consists of a laser tube, a tuning platform for grating and a stabilized current supply.   Output laser wavelengths can be selected easily by adjusting a special handle, the given CO laser can emit about 95 lines in the 5.2—6.3 μm spectral region under room temperature.   The sample cell is a multi–path absorption cell with a geometric length of 3 m, and with a maximum optical length of 300 m, the tem-perature of the cell can be controlled from —50—90°C.   The cell is equipped with a system for measuring vacuum, pressure, sample concentration, temperature, humidity, etc. and with an infrared spectrophotometer as well.

The transmittance $\tau(\nu)$ of a given laser line is obtained by the ratio method of con-trolling and measuring beams in order to eliminate errors caused by instability of the laser source and by variation of instrumental constants (Kong et al., 1983).   Then, the absorption coefficient $k(\nu)$ at selected laser frequency ν is obtained from the following equation:

$$\tau(\nu) = [I_1(\nu)/I_2(\nu)]/[I_1'(\nu)/I_2'(\nu)] = \exp[-k(\nu)u], \qquad (5)$$

where $I_1(\nu)$ and $I_1'(\nu)$ are signal intensities of the controlling beam at different time, re-spectively; $I_2(\nu)$ and $I_2'(\nu)$ are those of the measuring beam after passing through the vacuum cell and the cell filling a sample being measured, respectively; u is the sample concentration. Both NO and NO₂ are specially prepared, with their volume ratio being 1% and the
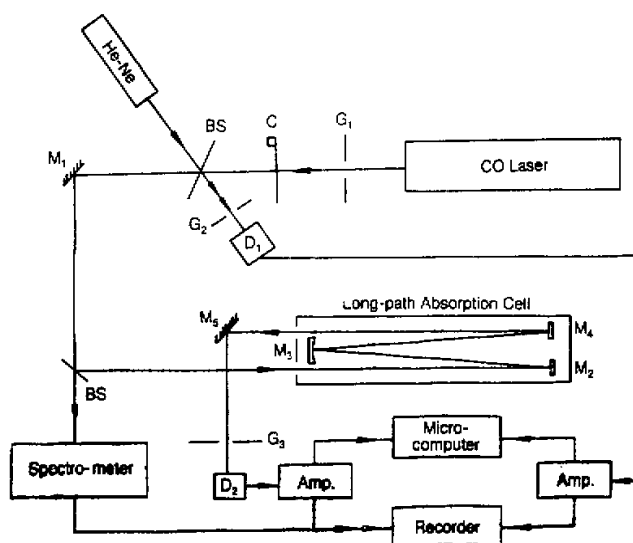
Fig. 1. Diagram of experimental equipment.

sample concentration ranging from 11 to 450 ppm. The optical lengths of 24 m, 96 m and 128 m are selected for NO measurements, and 12 m, 24 m and 48 m for NO_x. Before making experiment the absorption cell is evacuated and cleaned several times by dry nitrogen in order to decrease the effect of water vapour on measurements. Besides, the ultra-pure nitrogen is used as a broadening gas for all measurements. The sample temperatures varied within $22 \pm 0.5°C$ during the whole measurements.

IV. RESULTS AND ANALYSES

1. Absorption Coefficients

The vibration-rotational spectrum of NO $5.3 \mu m$ absorption band consists of two subbands. Effective vibrational and rotational constants of these two subbands are nearly identical, so that these two subbands are also identical. This effect leads to a double-line series of NO spectrum. The differences between the frequencies of these double lines are only a few thousandths of wavenumbers near the band center, but about two wavenumbers at the wings of the band. Line intensity of the subband $2\pi_{1/2}$ is about two times more than that of the subband $2\pi_{3/2}$. The wavelength of NO 5.3 μm absorption band is in the range of 1985 cm^{-1}—1777 cm^{-1}. The two subbands can easily be separated by using laser as a monochromatic radiation source according to the absorption properties of NO 5.3 μm band. As the wavelength range of XZJ-1 CO laser is limited, only the P-branch spectral lines of NO 5.3 μm band are studied. The selected laser frequencies and NO absorption coefficients obtained are listed in Table 1. The resonant absorption of 17 NO absorption lines was measured by means of CO laser in 1977 (Garside et al., 1977). For the same laser wavelengths the absorption coefficients obtained from both Garside's and our

Table 1. NO Absorption Coefficients

ν_{CO}(cm^{-1})	k_{NO}(atm-cm)$^{-1}$	k_{H_2O}(cm^2/g)	u_{NO}(atm-cm/km)
1784.153	0.41	40.26	34.37
1788.397	0.32	54.54	59.66
1801.120	0.34	71.63	72.88
1826.217	0.34	51.80	53.01
1829.592	1.21	362.40	104.70
1834.593	0.27	14.77	19.08
1838.708	0.24	12.49	18.52
1842.808	3.29	40.49	4.31
1847.131	0.33	27.20	28.67
1859.842	0.37	19.31	18.42
1863.655	1.07	8.71	2.86
1876.630	0.12	20.20	57.48
1880.901	0.63	2.29	1.28

studies are in good consistency.

NO$_2$ 6.2 μm absorption band is of an A-type one, its wavelengths range from about 1660 cm^{-1} to 1550 cm^{-1}, the high resolution spectrum in question has a very complicated structure, and the spectral lines seriously overlap and mix up with each other. NO$_2$ absorption coefficients at 29 frequencies of CO laser are given in Table 2. The absorption coefficients of water vapour k_{H_2O}(Kong et al., 1983) at the laser frequencies listed are also given in Table 1 and Table 2 in order to provide a reliable information for suitable

Table 2. NO₂ Absorption Coefficients

ν_{CO} (cm^{-1})	k_{NO_2} (atm-cm)$^{-1}$	k_{H_2O} (cm^2/g)	u_{NO_2} (atm-cm/km)	ν_{CO} (cm^{-1})	k_{NO_2} (atm-cm)$^{-1}$	k_{H_2O} (cm^2/g)	u_{NO_2} (atm-cm/km)
1575.200	8.3	76.57	3.22	1614.909	23.38	110.5	1.65
1580.778	10.1	62.63	2.17	1618.699	21.44	101.7	1.66
1582.880	15.5	33.09	0.75	1619.564	32.35	66.29	0.72
1584.359	8.6	25.57	1.04	1622.455	76.91	417.2	1.90
1587.907	45.6	18.69	0.14	1626.175	83.64	64.06	0.27
1590.457	32.4	35.77	0.39	1629.862	71.86	36.97	0.18
1595.609	53.6	106.8	0.70	1631.721	76.83	47.63	0.22
1597.929	28.7	34.06	0.41	1633.313	74.76	76.11	0.36
1599.488	41.2	18.83	0.16	1640.743	12.87	66.60	1.81
1601.614	19.2	19.00	0.35	1643.272	7.28	55.94	2.69
1603.386	55.4	33.89	0.21	1644.277	10.24	70.29	2.40
1605.265	41.4	22.03	0.19	1647.067	9.51	468.2	17.24
1607.252	54.9	22.23	0.14	1650.819	4.48	200.1	15.62
1611.084	50.4	62.31	0.43	1656.260	1.63	129.4	27.76
1612.487	50.7	33.86	0.23				

wavelength selection and reasonable data processing in the concentration determinations of
NO and NO_2. The u_{NO} in column 4 of Table 1 and u_{NO_2} in columns 4 and 8 of Table 2
are equivalent contents of NO and NO_2, respectively, and these values correspond to that
of the atmospheric transmittance with water vapour content of 0.35 $(g \cdot cm^{-3})/km$ in the
atmosphere (i.e. the middlelatitude winter atmosphere). It can be found from Tables 1 and
2 that there are three laser lines, for which the u_{NO} is less than 5 atm·cm/km, and nine
laser lines, for which u_{NO_2} is less than 0.3 atm·cm/km. It means that these laser lines are
less influenced by the water vapour and, therefore, can be used for NO and NO_2 measure-
ments in the actual atmosphere. According to Leithe (1971), the maximum values of the
NO background concentration in cities during the day usually vary from 0.13 to 0.37 ppm
(i.e. 0.013—0.037 atm·cm/km) in the atmosphere, but from 0.05 to 0.11 ppm for NO_2.
It is not difficult to understand that, in view of the low concentration and the water vapor's
influence, it is not suitable to monitor the background concentrations of NO and NO_2
in the actual atmosphere by using the present CO laser but some more advanced detection
techniques, such as the opto–acoustic method, and the gas correlation technique, can
make NO and NO_2 background determination realizable. In addition, for the sake of
studying the absorption properties of the whole NO 5.3 μm band, the CO laser should
be extended to the shorter wavelength side. Such kind of CO laser (usually the vibrational
quantum number is lower than 7) is also favourable to decrease the interference of water
vapour and increase the detection sensitivity.

2. Variation Characteristics of Absorption

According to the gas absorption theory, the gas absorption at a given wavelength is
proportional to its partial pressure in a certain range of pressure and gas concentration.
Figs. 2 and 3 give some examples o variations of NO and NO_2 attenuation coefficients
at some CO laser wavelengths with their partial pressures in the case of a total pressure of
760 mmHg. These examples distinctly show that in the case of unsaturated absorption the
variations of gas absorption with the partial pressure can well be described by a simple
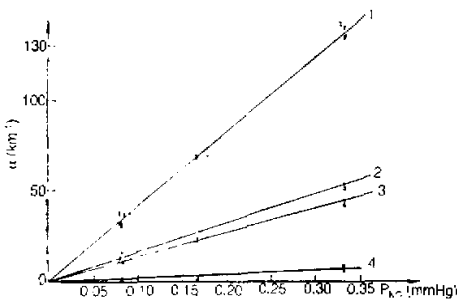linear relation.

Fig. 2. Variation of NO attenuation coefficient α
with partial pressure (total pressure P_t=760
mmHg).
1. λ=1842.808 cm⁻¹,   2. λ=1829.592 cm⁻¹,
3. λ=1863.665 cm⁻¹,   4. λ=1876.630 cm⁻¹.
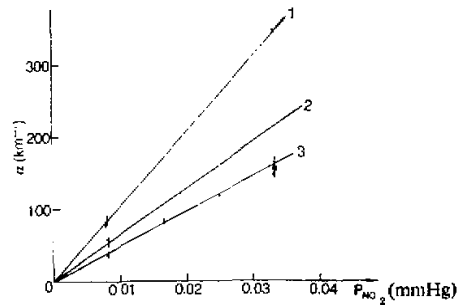
Fig. 3. As in Fig. 2, except for NO_2
1. λ=1633.313 cm⁻¹,   2. λ=1605.265 cm⁻¹,
3. λ=1619.564 cm⁻¹.

   The effect of total pressure on the gas absorption is also studied. As a fundamental content in the study of atmospheric molecular spectroscopy, it is important both in theory and in practical application, because the total pressure varies in a quite large range in the actual atmosphere. According to the single line absorption theory, in the case of unsaturated absorption, an absorption is weakened at the central part of a given absorption line due to pressure broadening, while at the wings of such a line the absorption seems to have a complicated character. The behaviors of NO and NO₂ absorptions with total pressure under the fixed partial pressure are presented in Figs. 4 and 5, respectively, indicating
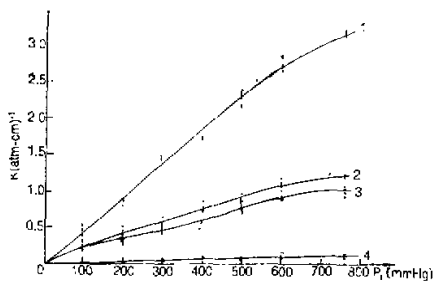

Fig. 4. Pressure broadening by N₂ in NO
         absorption. (P_{NO}=0.34 mmHg)
         1. λ=1842.808 cm⁻¹, 2. λ=1829.592 cm⁻¹,
         3. λ=1863.655 cm⁻¹, 4. λ=1876.630 cm⁻¹,
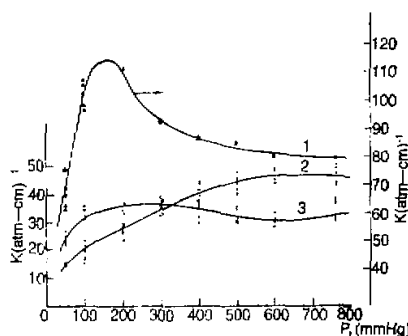
Fig. 5. Pressure broadening by N₂ in NO₂
         absorption. (P_{NO_2}=0.033 mmHg)
         1. λ=1633.313 cm⁻¹, 2. λ=1605.265 cm⁻¹,
         3. λ=1619.564 cm⁻¹.

that, for selected CO laser lines, although their central frequencies are located exactly or nearly at the central part of the corresponding NO or NO₂ absorption lines, the variations of absorption for these laser lines are quite different. NO absorption for the selected four CO laser lines basically increases with the total pressure as shown in Fig. 4. This character is consistent with that for the wings of the absorption line. It means that either of the laser lines locates actually at wings of NO absorption lines or there are some other strong NO absorption lines near the resonant absorption line. The results in Fig. 5, where variations of NO₂ absorption for three laser lines are given, are more complicated than those in Fig. 4. For example, for the 1633.313 cm⁻¹ laser line, when the total pressure is less than 160 mmHg, its absorption coefficient sharply increases with the total pressure, interpreting the absorption character of the line wings. However, when the total pressure continuously goes up, the absorption coefficient begins to drop off. This complex situation may be explained by a spectral line broadening due to the pressure effect. It is well known that the width of a gas absorption line is larger than that of a laser emission line and, what is more, the foremer obviously widens itself with increasing total pressure. Therefore, the relative position of the laser line to the given absorption line profile may vary during the broadening process. And the laser line, which was originally located at the wing of the given absorption line, moves to the central part of the absorption line. As a result, the absorption at the laser line is weakened with the pressure broadening. Besides, it should be pointed out that the phenomenon of overlapping and mixing of NO₂ lines is quite serious (Cabana et al., 1976), that the absorption at a given laser line is generally of a total con-

tribution of many NO_2 absorption lines and that, therefore, the variations of absorption properties due to the pressure broadening at a given laser line would show a complicated behavior.

V. ERROR ANALYSIS

As mentioned above, errors caused by the instability of CO laser source and the variation of instrumental constants are eliminated by using the double–beam ratio method in our experiment, and thus the errors in our measurements are mainly caused by those in the detection of the sample concentration and in the data collection.

The sample pressure is measured by a liquid vacuum gauge: a mercury gauge is used when the sample pressure is greater than 33 mmHg and its accuracy is better than 0.5 mmHg; an oil gauge is used with the accuracy of about 1/30 mmHg when the sample pressure is less than 33 mmHg. In the course of the whole experiments the minimum value of the sample pressure is 0.83 mmHg, and the maximum relative error is about 4%, resulting in a relative error of no more than 2% for a transmittance detection and another error of no more than 5% for the absorption coefficient.

During data processing, the manually data–collection from a record spectrum curves may lead to a maximum error of about 5% in the transmittance determination.

Since there is a wide range of absorption coefficients, and the different values of a sample's partial pressure are used, it is beyond doubt that there exist different values of the errors for different absorption coefficients. Taking all the above-mentioned into account, the maximum relative error for all the absorption coefficients determined in our experiment is no more than 14%.

REFERENCES

Bair, C.H. et al. (1977), Measurement of HCI absorption coefficients with a DF laser, *Appl. Opt.*, 16: 97–100.
Cabana, A. et al. (1976), High resolution infrared spectrum of the ν_3 and $\nu_2+\nu_3-\nu_2$ bands of NO_2, *J. Molec. Spectrosc.*, 59: 13–27.
Garside, B.K. et al. (1977), Resonance absorption measurements of NO with a line-tunable CO laser, *Appl. Opt.*, 16: 398–402.
Kong Qinxin et al. (1983), A study on atmospheric transmittance for 86 CO laser emission lines, *Scientia Atmospherica Sinica*, 7: 102—108 (in Chinese with English abstract).
Leithe, W. (1971), The Analysis of Air Pollutants, Ann Arbor Science Publishers, Inc.
Patel, C.K.N. (1978), Laser detection of pollution, *Science*, 22: 157–173.