# Detection of Nitric Oxide by the Resonance Absorption Technique

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The resonance absorption method is described for detecting ppm concentrations of NO mixed with other gases. As source lamp for the emission of the NO $\gamma$ system, A $^2\Sigma^+$ — X $^2\Pi$, a hollow cathode discharge has been used operating in streaming air at low discharge current ($\sim 1$ mA). NO detection is achieved by a double-beam technique with single-beam optics. The experimental average absorption coefficient obtained for the $\gamma$ (0,0) band is compared with the calculated value. Relevant NO spectroscopic information is reported.

## I. Introduction

Nitric oxide is a very common atmospheric pollutant being produced in virtually all atmospheric combustion processes [1, 2]. Quantitative analysis of NO is therefore important in smog and combustion research as well as for effective air pollution control. A method is described for detecting ppm or less concentrations of NO as it exists in the exhaust of internal combustion or in ambient air.

In the resonance line absorption method, detection is achieved by measuring the average absorption of the source emission lines due to the same transition in the absorbing gas sample [3–5]. The averaging procedure is performed over the entire molecular band with the relative emission intensities of the individual rotational lines as weight factors. Principal advantages are its high selectivity and sensitivity compared with continuum absorption. The resolution need only be good enough to separate one molecular band from other neighbouring bands which eliminates the use of high-resolution monochromators. The resonance absorption method has been applied to the (0,0) band of the NO $\gamma$ system (A $^2\Sigma^+ -$ X $^2\Pi$) at 2262 Å, the most longward absorption band in the UV spectral region [6].

## II. Source

The resonance absorption method requires a source of $(v', v'' = 0)$ band emission which is not overlapped by other bands, with known rotational distribution and Doppler temperature preferably close to room temperature.

The source should be optically thin and must have an adequate intensity which is stable over long periods of time. As NO source lamp which meets these rather stringent requirements, a hollow cathode discharge has been used operating in streaming air at about 1 torr and at a discharge current in the order of some mA. Due to the small power consumption ($\lesssim$ 1 Watt), the Doppler temperature of the source remains near room temperature. The NO source has an extremely constant output, typical long-term drifts over several days are below 1 per cent.

### *Rotational Distribution*

In order to obtain the rotational distribution of the NO source, high-resolution spectrograms were taken in the second order of a Jarrell-Ash 5m Ebert spectrograph at a reciprocal dispersion of $\sim 0.8$ Å/mm (30 $\mu$ slit width) [7]. According to a $^2\Sigma - {}^2\Pi$ transition, there are 12 rotational branches in these bands [8]. However, because of the small spin splitting in the A$^2\Sigma^+$ state [$0.0028 (N + 1/2)\,\mathrm{cm}^{-1}$, see [9]] compared to the Doppler width ($0.10\,\mathrm{cm}^{-1}$ for $T = 300$ K), four pairs of lines can be regarded as completely unresolved and treated as a single line. The rotational distribution in the zero vibrational level of the NO molecules in the A$^2\Sigma^+$ state is evaluated in Fig. 1 using the two most intense branches of the $^2\Sigma - {}^2\Pi_{3/2}$ subband, $P_2$ and $Q_2$, which are overlapped by the $^PQ_{12}$ and $^QR_{12}$ (satellite) branches, respectively [10]. The rotational temperature is obtained in the usual way by plotting the log of the intensities $I$ of individual rotational lines divided by their line strengths $S_{J'J''}$ versus the corresponding rotational energies $E_r$.

The Hönl-London factors $S_{J'J''}$ are calculated for a doublet-doublet transition, $\Delta\Lambda = 1$, in the general coupling case from formulas derived by Kovacs [11].

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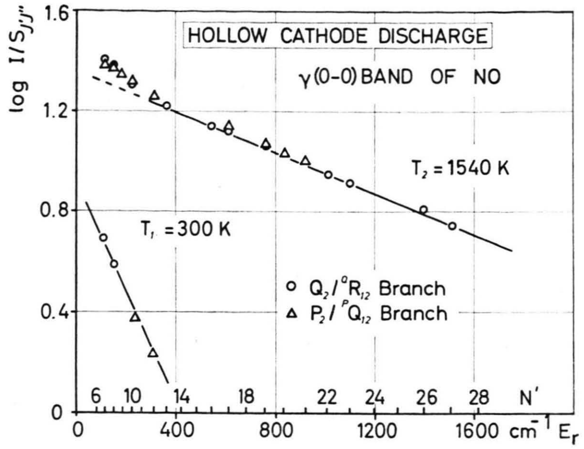

Fig. 1. Rotational distribution of NO ($A\,^2\Sigma^+$), $v'=0$, in a hollow cathode discharge.

The rotational energies for the $^2\Sigma$ state ($v'=0$) are given by (see Herzberg[8])

$$E_r = B_0' N(N+1) - D_0' N^2 (N+1)^2 \qquad (1)$$

with $B_0' = 1.9868\ \mathrm{cm}^{-1}$, $D_0' = 5.4 \cdot 10^{-6}\ \mathrm{cm}^{-1}$ from Ref.[12]; $J = N - 1/2$ for the $^2\Sigma - {}^2\Pi_{3/2}$ subband.

From the slope of the Boltzmann straight line at high $N$ values, a rotational temperature of 1540 K can be deduced. The difference in intensity at low $N$ values between the observed intensities and that of the extrapolated Boltzmann distribution is due to a second group of molecules which is characterized by a Boltzmann distribution of about 300 K corresponding to the Doppler or gas temperature of the source *. It has been shown for other diatomics like OH, CH and $C_2$ that the reason for this behaviour is due to two different excitation processes[13–15].

1. The high rotational temperature of 1540 K of the first ("hot") group of molecules is an indication that NO ($A^2\Sigma^+$) is formed via a three- or four-atomic collision intermediate, e. g. by dissociative recombination of $N_2 + O$, $O_2 + N$, $N_2^*$ (or $N_2^+$) $+ O_2$ or by electronic energy transfer e. g. $N_2\,(A^3\Sigma_u^+)$ $+ NO$. The nonthermal rotational distribution of diatomic species split from these collision intermediates can be explained by a statistical model on the basis of conservation of angular momentum throughout the splitting process[15].

2. The gas temperature of about 300 K of the second ("cold") group of molecules is observed for electron excitation of ground state NO molecules which are thermalized by relaxation. (For details of energy transfer of NO, see Ref.[16, 17].) A rotational distribution close to room temperature is also expected if NO ($A\,^2\Sigma^+$) molecules are populated by transfer from the $C\,^2\Pi$ state (C-A transition[18]) formed by radiative recombination of thermal $N + O$ atoms in a flowing afterglow[19]. It has been shown by Mandelman and Carrington[4] that the rotational distribution of NO ($C\,^2\Pi$) for this kind of NO formation corresponds to room temperature.

In addition it can be deduced from Fig. 1 that formation of NO ($A\,^2\Sigma$) molecules according to reaction scheme 1) is about 15 times as frequent as by 2) which explains the high efficiency of the NO source under optimized experimental conditions.

The rotational distribution observed will be of importance both for the extension of the resonance absorption method to a double-beam technique (Sect. III) and for the calculation of the average band absorption coefficient (Section IV).

## III. Measuring Method

### *A) Double-beam Technique*

Transmittance $T(\nu)$ is usually defined in terms of the optical depth $\tau$ by the Lambert-Beer law[3]

$$T(\nu) = I(\nu)/I_0(\nu) = \exp(-\tau)\,; \quad \tau = p\,k_\nu\,x \qquad (2)$$

where $k_\nu$ is the absorption coefficient, $p$ the partial pressure of the absorbing gas, $x$ the length of the absorbing path.

Based on the resonance absorption method, a schematic diagram of the monitoring instrument[20] is shown in Figure 2. In order to eliminate errors due to intensity fluctuations of the source or interfering absorption e. g. by coexisting molecular compounds or scattering of particles, the ratio of the transmitted $I(\nu)$ and the incident intensity $I_0(\nu)$ is determined by a double-beam technique in single-beam optics. The reference beam is obtained by passing the NO emission of the source alternately through a NO gas filter of high optical depth ($x\,p \cong 3$ mm · atm NO). Due to the high rotational temperature of 1540 K of the source, emission lines from high rotational levels will pass the NO gas layer nearly unfiltered. The total intensity of the reference beam thus obtained is about 10% of that of the measuring beam. The source radiation is collimated by a spherical mirror and passed through the sample cell. The transmitted radiation is focused onto a small monochromator or an equivalent inter-

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* The effect observed should not be confused with deviations which can occur due to incomplete resolution at low $N$ values near the band head.

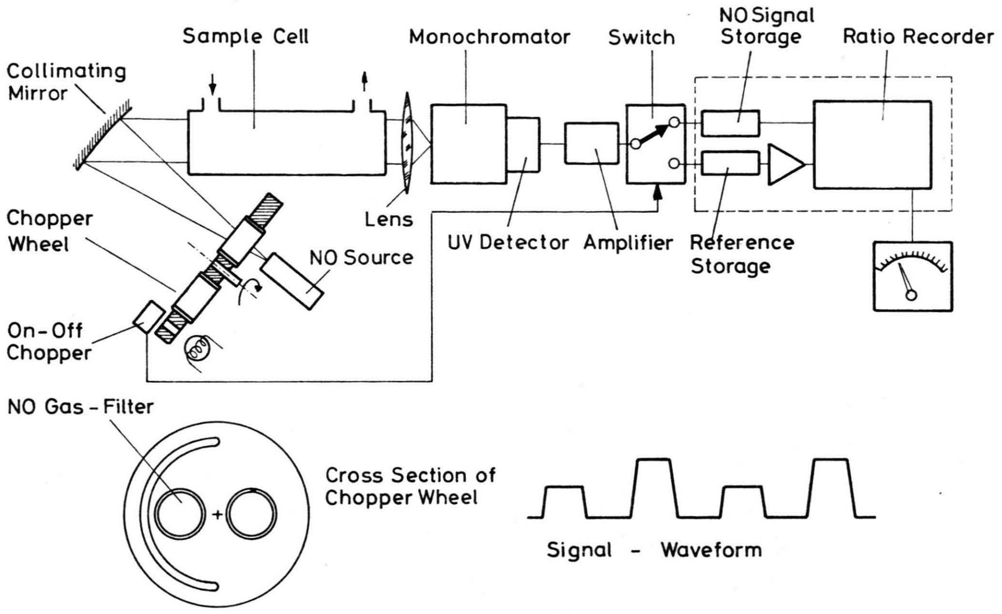

Fig. 2. Schematic diagram of the NO detector.

ference filter and detected by a photomultiplier. The resulting a-c detector output is further amplified. An a-c signal obtained from an on-off chopper mounted in front of the chopping wheel, drives a CMOS switch to positions corresponding at any instant to the measuring or reference source light. The corresponding potentials $V_1$ and $V_2$ are stored in the storage elements, and their ratio can be calibrated directly in units "ppm NO".

### *B) Calibration*

The experimental absorption coefficient of NO for the $\gamma(0,0)$ band is obtained, according to Eq. (2), from optical density curves plotting $\log(I_0/I)$ versus the concentration of NO (see Figure 3). The path length was kept constant since it has been shown that the observed band absorption depended only on the product of NO partial pressure and path length. For higher accuracy, the $k$ values (optical depth $\rightarrow 0$) were determined from the linear region of the experimental absorption curves (0 to 10% absorption). The slope of these straight lines appear in Fig. 3 as the asymptotes to the density curves.

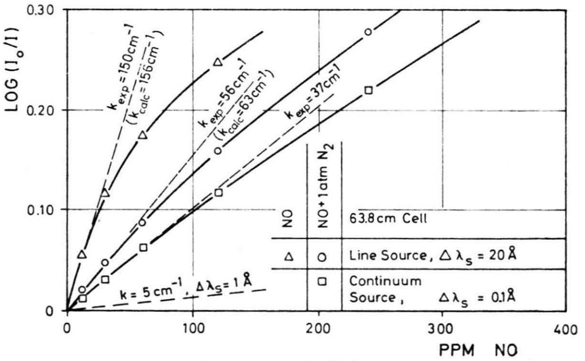

Fig. 3. Optical density curves (cell length 63.8 cm). △ Low pressure sample, resonance absorption, bandwidth 20 Å; ○ Pressurized sample (1 atm $N_2$), resonance absorption, bandwidth 20 Å; □ Pressurized sample (1 atm $N_2$), continuum absorption, bandwidth 0.1 Å.

At low pressure (pure Doppler broadening), a value of 150 $\mathrm{cm^{-1}\,atm^{-1}}$ is obtained. If the NO samples are pressurized by 1 atm of $N_2$, the average absorption coefficient is decreased to 56 $\mathrm{cm^{-1}\,atm^{-1}}$ due to pressure broadening.

For comparison, continuum absorption with a resolution of ~0.1 Å, yields a value of 37 $\mathrm{cm^{-1}\,atm^{-1}}$ for the ${}^{0}P_{12}$ band head, indicating that the sensitivity is lower even with a high-resolution monochromator. With a 1 Å resolution, the effective absorption coefficient is about 5 $\mathrm{cm^{-1}\,atm^{-1}}$. For comparison, the $k$ value for the NO fundamental at 5.25 $\mu$m is about 2.35 $\mathrm{cm^{-1}}$, see [21].

Minimum detectable concentration with a half-meter cell is about 1 ppm which can be easily reduced to 0.1 ppm by using a multiple reflection cell (10 traversals). In addition, the $NO_2$ component can be measured via a $NO_2$ thermal converter where $NO_2$ is thermally dissociated to NO.

In order to establish the usefulness of the NO detector for continuous monitoring, it has been tested when installed in the automobile exhaust sampling train and for point sampling of gas from hydrocarbon-air flames [22]. With the high-intensity version of the NO source lamp (discharge current several hundred mA), the resonance absorption technique has been applied to kinetical spectroscopy (bandwidth 1 MHz).

## IV. Computation of the Band Absorption Coefficient

### *A) General Theory*

The average absorption coefficients have been calculated in order to verify the experimental results. The calculation to evaluate the fractional absorption of the band requires the evaluation of the fractional absorption for each individual rotational line, the summing and averaging for all transitions over the entire band with the relative intensities of the emission band as weight factors [4].

The integrated absorption coefficient of a rotational line is related to its oscillatory strength $f^{v'v''}_{J'J''}$ by the equation [23, 24]

$$\int_{\text{line}} k_\nu \, \mathrm{d}\nu = \frac{\pi e^2}{m c^2} f^{v'v''}_{J'J''} N(J'') ; \tag{3}$$

$m$ and $e$ are mass and charge of the electron, respectively, $c$ is the velocity of light.

$$f^{v'v''}_{J'J''} = f_{v'v''} S_{J'J''}/(2J''+1) . \tag{4}$$

The band absorption oscillator strength $f_{v'v''}$ for the NO-$\gamma(0,0)$ band is taken from Ref. [25] to be $4.01 \cdot 10^{-4}$. The Hönl-London factors $S_{J'J''}$ for the 12 branches of the $^2\Sigma^+ - {}^2\Pi$ system are calculated by the formulas derived by Kovacs [11].

$N_1(J'')$ and $N_2(J'')$ are the populations for the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ components of the ground state, respectively

$$N_{1,2}(J'') = n_0 \frac{(2J''+1)}{Q} \exp\{-h c F_{1,2}(J'')/k T\} \tag{5}$$

where $n_0 = 2.69 \cdot 10^{19}$ molecules/cm$^3$.

$F_{1,2}(J'')$ are the term values given by the Hill and Van Vleck formula [8]

$$F_{1,2}(J'') = B_0''\{(J''+1/2)^2 - 1 \mp (1/2)[4(J+1/2)^2 + Y(Y-4)]^{1/2}\} - D_0''(J''+\tfrac{1}{2}\mp\tfrac{1}{2})^4 \tag{6}$$

where $Y = A_0/B_0''$; $A_0 = 123.18$ cm$^{-1}$, $B_0'' = 1.6956$ are the spin-orbit splitting and rotational constants, respectively, $D_0'' = 5.4 \cdot 10^{-6}$ cm$^{-1}$ (from Ref. [12]).

The upper sign $(-)$ refers to levels of the $^2\Pi_{1/2}(F_1)$ and the lower sign $(+)$ to the $^2\Pi_{3/2}$ state $(F_2)$. $Q$ is the internal partition function which was evaluated according to

$$Q = 2 \sum_{J''} (2J''+1)[\exp\{-h c F_1(J'')/k T\} + \exp\{-h c F_2(J'')/k T\}] . \tag{7}$$

The factor 2 arises from the $\Lambda$-doubling.

For a Doppler line (in practice corresponding to 0 – 5 torr), the left-hand side of Eq. (3) can be integrated [3]

$$\int_{\text{Doppler line}} k_\nu \, \mathrm{d}\nu = \tfrac{1}{2}(\pi/\ln 2)^{1/2} k_0 \Delta\nu_{\mathrm{D}} \tag{8}$$

where $k_0$ is the absorption coefficient at the center of the line and $\Delta\nu_{\mathrm{D}}$ is the Doppler width given by

$$\Delta\nu_{\mathrm{D}} = \frac{2}{c} (2 R \ln 2)^{1/2} \nu_0 (T/M)^{1/2} \tag{9}$$

yielding 0.098 cm$^{-1}$ (0.005 Å) for $T = 300$ K.

The evaluation of the "true" absorption coefficient incorporating Doppler and collisional broadening is done by the Voigt profile expression, in the same way as in atomic absorption spectroscopy

$$k_\nu = k_0 \, \delta(a, v) \tag{10}$$

where $\delta(a, v)$ is the value of the Voigt profile function [3, 26, 27]. The values "$a$" and "$v$" depend on the Doppler and collision width of the absorber; the pressure broadening collision diameter of NO was taken from Ref. [28] to be 3.8 Å.

### *B) Results and Discussion*

The results of the computation of $k_0$ at the center of the lines according to Eqs. (3) – (9) is illustrated in Fig. 4 for the 8 branches of the $\gamma(0,0)$ band of NO at 300 K.

The corresponding absorption cross sections $\sigma_0$ are related to the absorption coefficients by

$$k_0 = n_0 \, \sigma_0 . \tag{11}$$

The fractional absorption of each rotational line was calculated in the limit of small optical depth ($\tau \ll 1$, linear region of absorption curve) by integrating over the source line which was assumed to be a Doppler profile of 300 K. Averaging over the band includes lines with $J''$ up to 27.5 in 12 branches assuming a rotational distribution of emission lines of 1540 K (see Figure 1). The calculation has been carried out for the two limiting cases of Fig. 3, for low pressure and for 1 atm total pressure. The cor-

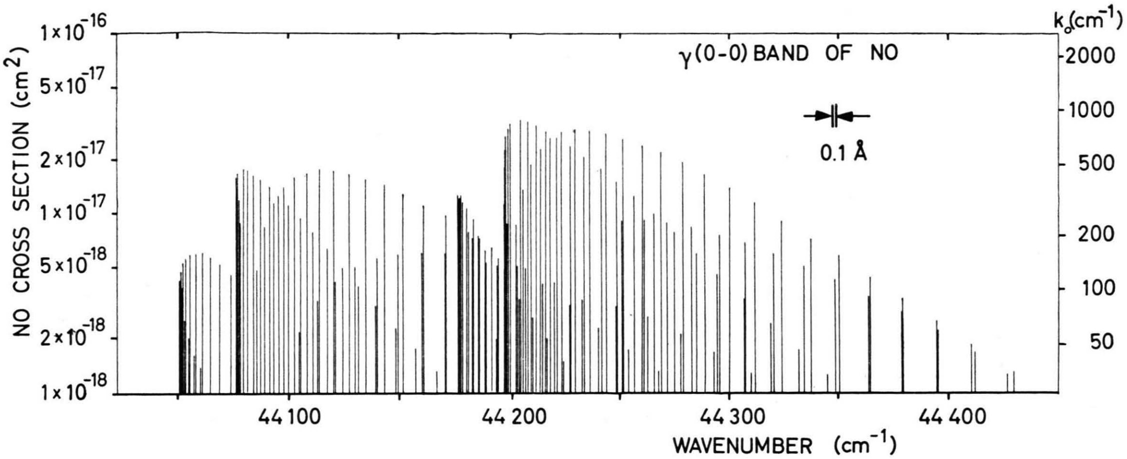

Fig. 4. Structure of the absorption of NO in the spectral range of the $\gamma$ (0,0) band at 300 K.

responding values for the average absorption coefficient obtained are 156 and 63 cm$^{-1}$, compared with the experimental values of 150 and 56 cm$^{-1}$, respectively.

The calculation is based on several assumptions. Line shift (between emitter and absorber) due to adiabatic interactions (Van der Waals) has been ignored. It has been assumed that the spin-rotation splitting in the $A^2\Sigma$ state is negligible compared with the absorber line width (see Section II). This assumption of exact overlap of pairs of lines will lead to an overestimate of fractional absorption. On the other hand, neglecting overlap of lines which occurs above all in the band heads, will introduce errors which have the opposite effect. Mandelman and Carrington[4] give a detailed calculation for the effects of line overlap and perturbations for the $\delta(0,0)$ band of NO. They determined the overlap contribution to be less than 20%, the final (recommended) results lie within about 10% of the uncorrected values.

On the basis of this discussion it is evident that the calculation is approximate and may be in error by about 20%.

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