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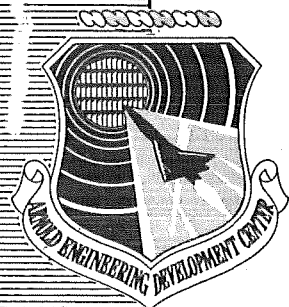
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# Reevaluation of Nitric Oxide Concentration in Exhaust of Jet Engines and Combustors

J. D. Few and H. S. Lowry, III  
ARO, Inc.

August 1981

Final Report for Period April 1 – September 1, 1980

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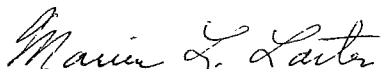
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## ERRATA

AEDC-TR-80-65, August 1981  
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REEVALUATION OF NITRIC OXIDE CONCENTRATION  
IN EXHAUST OF JET ENGINES AND COMBUSTORS

J. D. Few and H. S. Lowry, III, ARO, Inc.

Arnold Engineering Development Center  
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Arnold Air Force Station, Tennessee 37389

The following corrections should be noted and made in copies of this report. Throughout the report, the broadening parameter should be noted by a script capital "A":  $\mathcal{A}$ . This symbol has been printed erroneously as a printed capital (A) or a printed lowercase (a) letter. Errors have been noted for pages 7, 9, 12, and 13.

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<p>Several measurements of nitric oxide (NO) concentrations in the exhaust of jet engines and combustors by probe sampling and ultraviolet (UV) resonance absorption have been reported. Generally, the optically determined concentrations have exceeded the probe determined values appreciably. The theoretical basis for the determination of the NO concentration from absorption measurements has recently been reexamined, and the values</p>		

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### 20. ABSTRACT (Continued)

previously reported were redetermined. This report presents revisions to the original theory, determination of parameters to be used in the theory from new experimental data, and results of redetermination of the NO concentration for the several cases. Upon reexamination, the parameter  $a$  (the ratio of collisional plus natural half-width to the Doppler half-width) was found to obey the relationship  $a = C P/T_0^{1.5}$  where  $P$  is the pressure in atmospheres,  $T$  is the temperature in K, and  $C$  is a constant. The value of  $C$  was found to be  $3.81 (\pm 0.40) \times 10^4 \text{K}^{1.5}/\text{atm}$ . The major conclusion of previous studies remains unchanged, namely, that optically determined NO concentrations may be a factor of 5 larger than probe determined values or may be the same, depending on the combustion gas flow conditions and/or probe design. However, certain optically determined NO concentrations varied by as much as 46 percent from previously reported values because of alterations made to the theory and parameters.

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## **PREFACE**

The work reported herein was conducted by the Arnold Engineering Development Center (AEDC), Air Force Systems Command (AFSC). The results of the test were obtained by ARO, Inc., AEDC Group (a Sverdrup Corporation Company), operating contractor of the AEDC, AFSC, Arnold Air Force Station, Tennessee, under Project Number P32I-86. The project manager was Capt. K. H. Leners, USAF. The manuscript was submitted for publication on October 22, 1980.

The authors wish to express their sincere appreciation to H. N. Glassman for his work in coding the programs.

Messrs. Few and Lowry are presently employed by Calspan Field Services, Inc., AEDC Division.



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## 1.0 INTRODUCTION

Several measurements of nitric oxide (NO) concentration in the exhaust of jet engines and combustors by probe sampling and ultraviolet (UV) resonance absorption have been reported (Refs. 1 through 4). The optically determined values of concentration have appreciably exceeded the probe determined values. In the present reexamination of the theoretical basis for determining the NO concentration from absorption measurements, the values previously reported have been redetermined. This report presents revisions to the original theory, determination of parameters to be used in the theory from new experimental data, and the results of redetermination of the NO concentration for several cases.

The UV resonance absorption method for NO concentration measurement involves matching a calculated transmittance at the principal bandhead of the (0,0)  $\gamma$ -band of NO through a medium of known temperature, pressure, and major species concentration distribution to a measured transmittance of the NO (0,0)  $\gamma$ -band emitted from a gas discharge tube. The calculation is made through use of a line-by-line radiative transfer model (Ref. 5). Dodge and Dusek (Ref. 6) recently reported both discrepancies in the original model and some less significant computer programming errors which they found while attempting to use the computer code. These discoveries led to a revision of the original model and redetermination of critical parameters (Ref. 7). It is necessary to reconsider the previously reported data in light of the revised model and newly determined parameters.

The radiative transfer model depends, critically, on two source parameters and two parameters characteristic of the absorbing molecule. The source parameters are the peak line intensity distribution and the Doppler half-width of the lines emitted by the electric discharge source. The absorber parameters are the absorption coefficient at line center and the collisional broadening line width. The discrepancy in theory (Ref. 5) was contained within the expression for the absorption coefficient, namely, in the treatment of the rotational partition function and normalization of the band oscillator strength. The reported broadening parameter was experimentally determined, based on the validity of that model and, thus, was in error. The source line intensity distribution was measured in the previous work, and the source translational temperature was assumed to be slightly greater than room temperature.

In the present work the theoretical model has been revised to include (1) the correct formulation of the state population, (2) the correction of numerical errors, and (3) the incorporation of the latest values of NO  $\gamma$ -band line positions and oscillator strengths (Ref. 7). A laboratory program has also been conducted that involved using two absorption cells — a high-temperature cell and a high-pressure cell with respective path lengths of 75.57 cm and 51.11 cm. The high-temperature cell was operated over a temperature range of from

295 K to 750 K, and the high-pressure cell was operated at pressures ranging from 0.0 to 3.4 atm.

The source temperature was determined from these data and with the aid of the corrected model. With this new value of source temperature, the model was used to determine that value of the collisional broadening parameter which best fit the absorption data over a range of pressures and temperatures. The results of this laboratory study have shown a nonlinear temperature dependence of the collisional broadening not previously reported. Also, these data prompted a reexamination of the relationship of pressure and temperature to the broadening parameter ((1)).

Optical measurements of nitric oxide concentrations have been previously reported for a number of combustion sources. The measurements involving engine combustors and jet engine exhausts have been recalculated using the corrected model and the new parameters; the results are included herein. A comparison of these old and new optically determined values reveals some differences, but the original large discrepancy with probe measurements remains for high-velocity combustor exhausts (Ref. 2) and jet engine exhausts (Refs. 1 and 4). It should be noted that the results of applying the newly found temperature dependence of the collisional broadening to the burner and combustor measurements of the interagency NO program (Refs. 6 and 7) have not been included.

## 2.0 REVIEW OF MODEL

### 2.1 THEORY

A theoretical model for the transmission of Doppler-broadened resonance line radiation through absorbing media with combined Doppler and pressure broadening was given by Davis, McGregor, Few, and Glassman (Ref. 5) with application to the  $\gamma$ -band of NO. The formulation given in Ref. 5 was incorrect in that (1) Hund's case (b) statistics (Ref. 8) were used, (2) the spin splitting was not properly taken into account, and (3) the normalization of the line oscillator strength was inconsistent with the literature (Refs. 9 and 10). The method of calculation of the partition function in the model has now been changed to conform to the angular momentum coupling intermediate between Hund's cases (a) and (b). A brief review of the theory is presented in the following.

The transmission,  $\tau$ , of an isolated, Doppler-broadened emission line through a homogeneous medium of length,  $\ell$ , is given by

$$\tau_j = I_{\nu_j}^{00} \int_0^\infty \exp \left\{ - \left[ \frac{2(\nu - \nu_j^0)}{(\Delta_s \nu_j)_D} \sqrt{\ell n 2} \right]^2 \right\} \exp \left[ -k(\nu) \ell \right] d\nu \quad (1)$$

where  $I_{\nu_j}^{00}$  is the intensity of the source line at line center,  $\nu_j^0$  is the frequency at line center,  $(\Delta_s \nu_j)_D$  is the half-width of the Doppler-broadened line, and  $k(\nu)$  is the monochromatic absorption coefficient of the medium. The half-width of the source line depends on the source temperature and is given by

$$(\Delta_s \nu_j)_D = 2\nu_j^0 \sqrt{\frac{2 \ln 2 \kappa T_s}{M_s c^2}} \quad (2)$$

where  $M_s$  is the molecular weight of the emitting molecule,  $T_s$  is the source temperature,  $\kappa$  is Boltzmann's constant, and  $c$  is the speed of light.

The absorption coefficient,  $k(\nu)$ , contains contributions,  $k_i(\nu)$ , from all lines near the frequency,  $\nu_j^0$ . Each of these lines will be broadened both by the Doppler effect and by collisions. The absorption coefficient of the  $i$ th line is given by the Voigt profile,

$$k_i(\nu) = k_i^0 \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\ell e^{-y^2}}{(\ell^2 + (\omega_i - y)^2)} dy \quad (3)$$

where  $k_i^0$  is the centerline Doppler absorption coefficient of the  $i$ th line, and the broadening parameter,  $a$ , is a parameter proportional to the ratio of the collision-broadening half-width,  $(\Delta_a \nu_i)_L$ , to the Doppler-broadened half-width,  $(\Delta_a \nu_i)_D$ , in the absorbing medium. The broadening parameter,  $a$ , equation is as follows:

$$\ell = \frac{(\Delta_a \nu_i)_L}{(\Delta_a \nu_i)_D} \sqrt{\ln 2} \quad (4)$$

The parameter  $\omega_i$  in Eq. (3) is the Doppler function

$$\omega_i = \frac{2(\nu - \nu_i^0)}{(\Delta_a \nu_i)_D} \sqrt{\ln 2} \quad (5)$$

It can be shown (Refs. 6 and 11) that

$$\ell = C p/T^n \quad (6)$$

where  $p$  is the pressure,  $T$  is the temperature,  $C$  is a constant for any given mixture of broadening species, and  $n$  is the temperature dependence exponent. The appropriate absorption coefficient in Eq. (1) must include the contributions due to all absorbing lines that overlap the source line,  $j$ ; thus,

$$k(\nu) = \sum_i k_i(\nu) = \sum_i \frac{k_i^0}{\pi} \int_{-\infty}^{\infty} \frac{Q e^{-y^2}}{Q^2 + (\omega_i - y)^2} dy \quad (7)$$

There may be several emission lines within a given instrument bandpass,  $\Delta\nu_1$ . The contributions of each of these lines must be summed to obtain the transmission within the given instrument bandpass. Thus, the transmissivity within the bandpass,  $\Delta\nu_1$  is given by substituting Eq. (8) into Eq. (1), summing over the emission lines, j, and dividing by the total intensity of the source within the bandpass as follows:

$$\tau_{\Delta\nu_1} = \frac{\sum_j I_{\nu_j^0} \int_{\Delta\nu_1} \exp \left\{ - \left[ \frac{2(\nu - \nu_j^0)}{(\Delta_s \nu_j)_D} \ell_n 2 \right]^2 \right\} e^{-\ell k(\nu)} d\nu}{\sum_j I_{\nu_j^0} \int_{\Delta\nu_1} \exp \left\{ - \left[ \frac{2(\nu - \nu_j^0)}{(\Delta_s \nu_j)_D} \ell_n 2 \right]^2 \right\} d\nu} \quad (8)$$

where  $k(\nu)$  is given by Eq. (8).

The line center absorption coefficient for a single transition out of the 12 possible transitions from a given  $J''$  is given by

$$k_i^0 = \left( \frac{2e^2 \sqrt{\pi} \ell_n 2}{m_e c^2} \right) \frac{N(v'' J'' K'' p) f(n' v' J' K' n'' v'' J'' K'')}{(\Delta_a \nu_i)_D} \quad (9)$$

where i refers to the particular  $n' v' J' K' n'' v'' J'' L''$  transition in the  $A^2\Sigma, x^2\Pi$  v-band system of NO. The constants in parentheses are the electron charge, e, the electron mass,  $M_e$ , and the speed of light, c. The population of the  $v''$  vibrational level in the  $J'' K''$  rotational sublevel and one of the parity levels, p, (+ or -) of the  $2\Pi_Q$  state in the intermediate angular momentum coupling case between Hund's cases (a) and (b) is given by

$$\frac{N(v'' J'' K'' n p)}{N_{total}} = \frac{(2J'' + 1) \exp \left\{ \frac{-G(v'') + F_m(J'')}{\kappa T} \right\}}{2 \sum_v \left\{ \exp \left[ \frac{-G(v)}{\kappa T} \right] \sum_{m=1}^2 \sum_{J=\Omega_m}^{\infty} (2J + 1) \exp \left[ \frac{-F_m(J)}{\kappa T} \right] \right\}} \quad (10)$$

where T is the temperature,  $G(v'')$  is the vibrational energy ( $\text{cm}^{-1}$ ), and  $F_m(J'')$  is the rotational energy ( $\text{cm}^{-1}$ ) for either the  $2\Pi_{1/2}$  state ( $m = 1$ ) or the  $2\Pi_{3/2}$  state ( $m = 2$ ). For purposes of the population, calculation is approximated by the Hill and Van Vleck formulas (Ref. 8):

$$F_1 = B_v \left[ \left( J + \frac{1}{2} \right)^2 - 1 - \frac{1}{2} \sqrt{4 \left( J + \frac{1}{2} \right)^2 + Y(Y - 4)} \right] - D_v J^4 \quad (11a)$$

$$F_2 = B_v \left[ \left( J + \frac{1}{2} \right)^2 - 1 + \frac{1}{2} \sqrt{4 \left( J + \frac{1}{2} \right)^2 + Y(Y - 4)} \right] - D_v (J + 1)^4 \quad (11b)$$

where  $Y = A/B_v$  where  $A$  is the splitting constant,  $B_v$  is the inertial rotational constant, and  $D_v$  is the centrifugal rotational constant. The oscillator strength for the transition is given by

$$f(n' v' J' K' J'' K'') = \frac{S(J' K' J'' K'')}{2J'' + 1} \frac{\nu(J' K' J'' K'')}{\nu(v' v'')} f(v' v'') \quad (12)$$

where  $(J' K' J'' K'')$  and  $(v' v'')$  are the frequencies of the line and band centers and where the normalization for the Honl-London factors  $S(J' K' J'' K'')$  and the normalization of the band oscillator strength follow that of Tatum (Ref. 9) and are consistent with Pery-Thorne and Banfield (Ref. 10). The Honl-London factors are those of Earls (Ref. 12).

The line positions,  $\nu_j^0$ , previously used were those of Deesz (Ref. 13). Improved data have recently become available (Ref. 14), and these data have been correlated (Ref. 6) into a consistent formulation. These new line positions have been incorporated into the model.

The source parameters are the peak line intensity,  $I_{\nu_j^0}^0$ , and the Doppler half-width of the lines,  $(\Delta_s \nu_j)_D$ . It is sufficient to determine only the relative peak line intensity since any absolute magnitude will cancel in Eq. (8). The relative peak line intensity can be determined by direct measurement for resolved lines; the intensities of the unresolved lines can be determined from the upper state population implied by the measured line intensities. However, for low-pressure, Doppler-broadened source lines in the ultraviolet, direct measurement of either the half-width or the source temperature is difficult. Section 2.2 describes an indirect method of determining source temperature.

The absorber parameters are the absorption coefficient at line center,  $k_i^0$ , and the quantity  $A$ , related to the collisional broadening. If the temperature and density within the absorption path are known, then  $k_i^0$  is determined by Eq. (10) if the band oscillator strength,  $f(v' v'')$ , is also known. Thus, when  $k_i^0$  is known, the broadening coefficient,  $C$ , of Eq. (6) can be determined from the value of broadening parameter,  $\mathcal{A}$ , required to obtain a match between the measured transmissivity and the transmissivity calculated from the model based on Eqs. (8) through (12).

Successful application of the model represented by Eqs. (8) through (12) requires a known source line intensity distribution, source temperature, band oscillator strength, and broadening coefficient.

## 2.2 PARAMETERS

The model represented by Eqs. (8) through (12), together with carefully controlled laboratory experiments, can be used to determine the source temperature,  $T_s$ , and the broadening parameter,  $\mathcal{A}$ , when the source line positions and intensities are specified and the band oscillator strength is known. Careful measurements of oscillator strength for the NO molecule have been made with several methods (e.g., Refs. 10, 15, and 16). Review of these measurements shows that the value [Hassan et al. (Ref. 15)] of  $4.09 \pm 0.1 \times 10^{-4}$  for the oscillator strength of NO is the most reliable.

### 2.2.1 Source Lines

The line positions of the (0,0) band of the  $\gamma$  system of NO as specified by Engleman (Ref. 14) have been adopted as the most accurate available. The source line intensity distribution of the AEDC capillary discharge lamp has been remeasured with resolution sufficient to identify many lines lying in each of the independent branches of the (0,0) band. No changes from the previously reported intensity distribution (Ref. 5) were found.

### 2.2.2 Source Temperature

Determining the effective source temperature hinges on the fact that at low pressure the transmissivity becomes independent of the other unknown parameter, the collision-broadening parameter. In the low-pressure limit, the combined Doppler- and collision-broadened absorption profile [Eq. (3)] reduces to a Gaussian profile whose half-width depends only upon the absorber temperature. Thus, if the absorber temperature and number density are known and if the measured value of oscillator strength is used, then the only unknown in Eq. (8) is the Doppler half-width of the source. This half-width is directly related to the source temperature through Eq. (2).

The experimental apparatus described in Ref. 5 was used to make a carefully controlled set of transmission measurements. A sequence of transmissivity measurements at the second bandhead was made over a range of pressures, with the NO number density and temperature held constant. In order to determine the source temperature, the transmissivity for a given number density and temperature was determined from the intercept of the transmissivity versus pressure curve (Fig. 1) in the limit of zero pressure (corresponding to  $\mathcal{A} = 0$ ).

Eq. (8), this value of transmissivity was used in the limit where  $\mathcal{A}$  approaches zero to determine the source temperature. The source temperature was adjusted to force a match between the calculated and extrapolated, measured transmissivities. A value of source temperature of  $950 \pm 25$  K was obtained by this method. Again, it should be noted that the source temperature is a characteristic of the lamp design and is expected to vary for different designs.

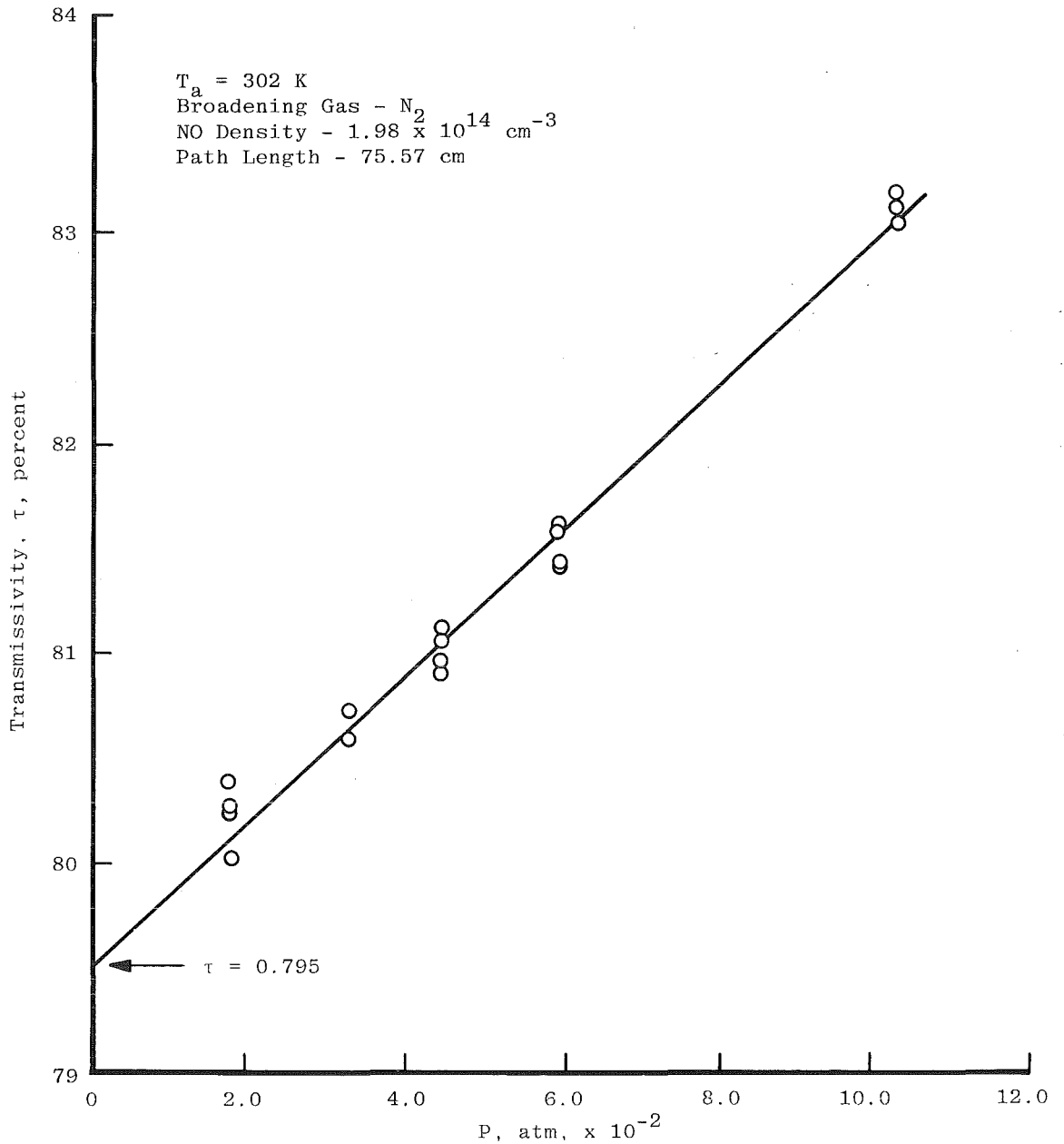


Figure 1. Least-squares fit to measured transmissivity versus pressure.

### 2.2.3 Broadening Coefficient

In the original work in which the broadening parameter,  $\ell$ , was reported (Refs. 5 and 17), a simple collisional theory was assumed in which  $n$  of Eq. (6) was set equal to unity. The data scatter, together with the influence of a mercury effect on the NO density caused by the presence of a McCleod gage connected to the absorption cell, obscured any nonlinear dependence of  $\ell$  on  $(1/T)$ . In more recent work (Refs. 7 and 18), data obtained for elevated temperature were insufficient to evaluate the temperature dependence; the Lorentz dependence ( $n = 1$ ) was again assumed. However, Dodge et al. (Ref. 6) had found that their transmission measurements on flat-flame, seeded  $H_2/O_2$  burners at elevated temperatures could best be correlated with a value  $n = 1.2$  in Eq. (6). This warranted additional investigation of the temperature dependence of the broadening parameter.

A series of experiments was performed in which known concentrations of NO were used, with  $N_2$  as a diluent gas, over a range of pressures (from 0.06 to 3.4 atm) and temperatures (from 295 to 750 K). Two absorption cells were constructed to accomplish this task. The high-temperature cell (quartz) and the high-pressure cell (stainless steel with quartz windows) had optical path lengths of 75.57 and 51.11 cm, respectively. In this investigation many data points were obtained from 295 K room temperature to 750 K for the determination of the temperature dependence exponent  $n$  for the NO  $\gamma$ -band. The measured values of transmissivity, together with Eqs. (8) through (12), were used to determine the value of  $A$  for each experimental condition. The value of  $A$  permits determining the exponent  $n$  according to  $A = C P/T^n$ . The value of  $n$  is obtained by plotting  $\ln A/p$  versus  $\ln T$ , where the slope is equal to  $n$  and the intercept is equal to  $\ln C$ . Figure 2 is a plot of  $\ln(A/p)$ , normalized to  $(A/p)_0$  at the fill conditions of the absorption cell, versus  $\ln T/T_0$ . The temperature dependence found from Fig. 2 was  $n = 1.5(\pm 0.2)$ ; i.e., the broadening parameter  $\ell$  obeys the relationship  $A = C P/T^{1.5}$ .

Figure 3 is a plot of  $\ell$  versus  $P/T^{1.5}$  or 175 data points showing the least-squares straight line fit to the data. The slope is another way of determining the value of  $C$ . From the data shown in Figs. 2 and 3, the value of  $C$  was determined to be  $3.81 (\pm 0.40) \times 10^4 K^{1.5}/\text{atm}$ .

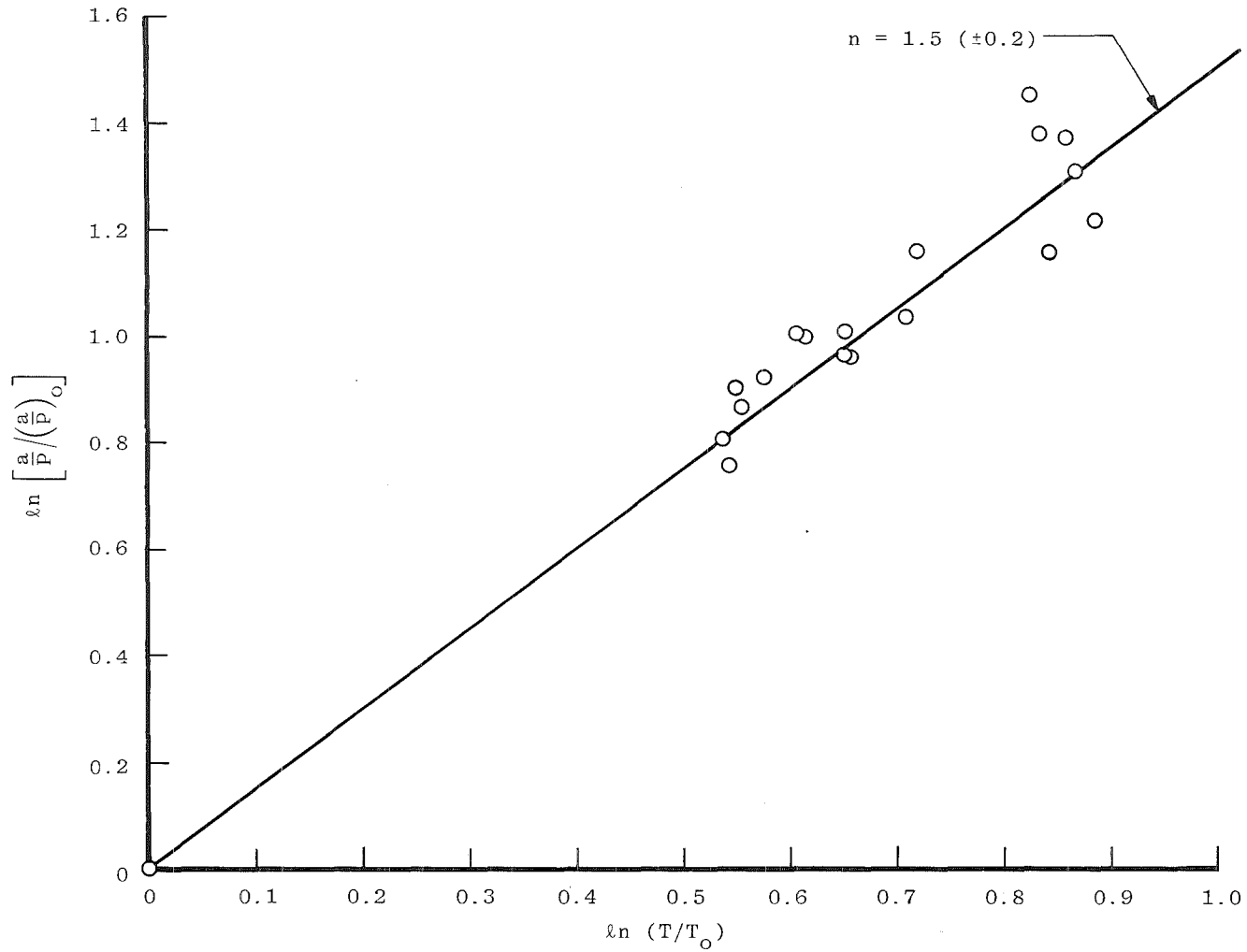


Figure 2. Determination of the temperature dependence exponent,  $n$ , for the NO (0,0)  $\gamma$ -band.

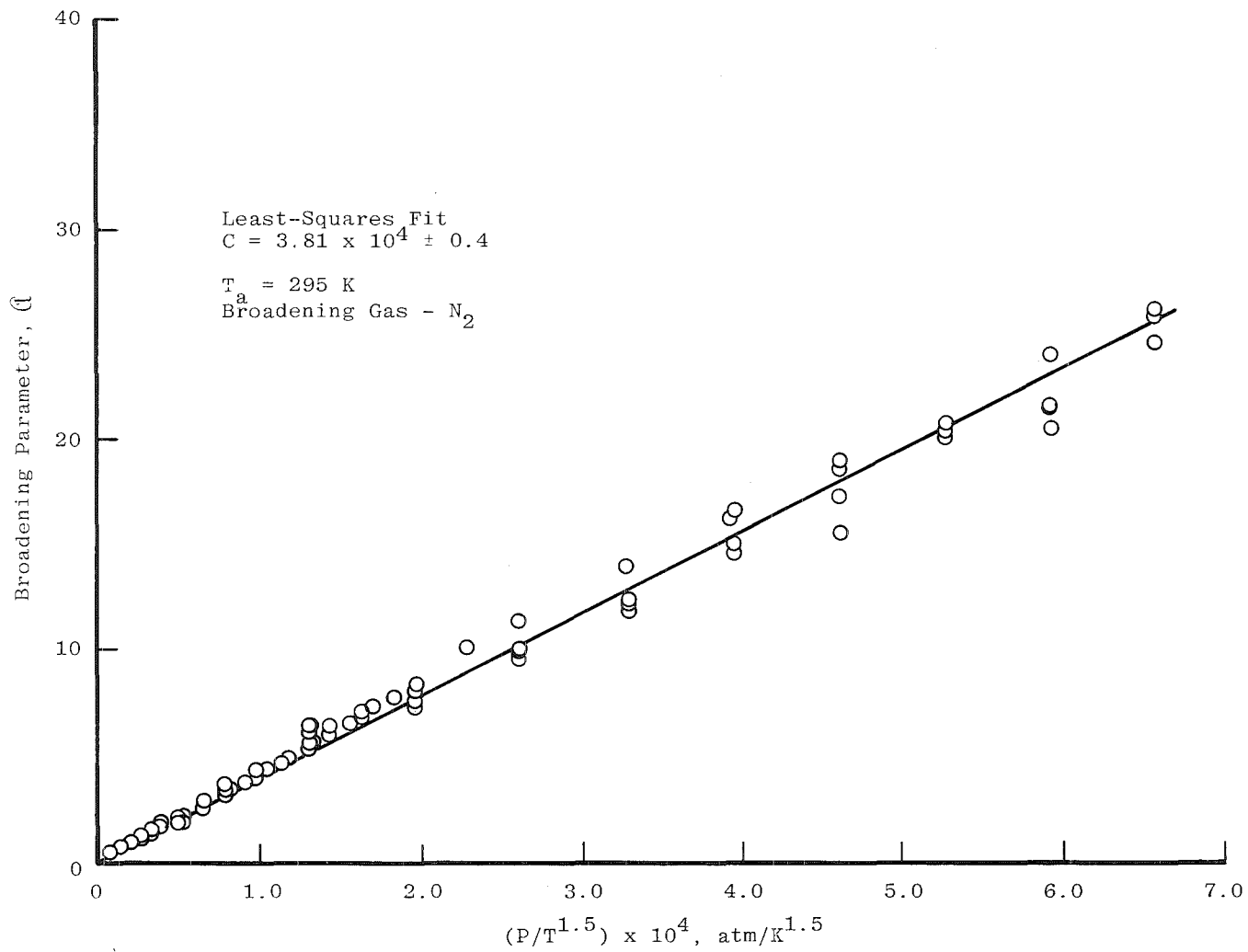


Figure 3. Values of the spectral broadening parameter,  $\bar{\nu}$ , as a function of  $P/T^{1.5}$  for the NO (0,0) band.

### **3.0 RESULTS OF REDETERMINATION OF NO CONCENTRATION FOR SEVERAL COMBUSTION SOURCES**

The absorption data for the following cases (Refs. 1 through 4) have been subjected to the revised theoretical model and computational procedure: (1) YJ-93 Turbojet Engine (Ref. 1), (2) Jet Engine Combustor Exhaust (Ref. 2), (3) Turbine Engine Combustor (Ref. 3), and (4) F101-GE-100 Turbofan Engine (Ref. 4). The results are presented and discussed in the following paragraphs.

#### **3.1 YJ-93 TURBOJET ENGINE (REF. 1)**

Reference 1 reports the results of a measurement program whose purpose was to study some of the constituents of the exhaust plume of a YJ93-GE-3 engine at simulated flight conditions. This was the first reported use of the NO narrow-line UV absorption technique in conjunction with a high-temperature combustion process. The transmission data were reduced to concentrations by extrapolation of laboratory calibration data and the assumption of Doppler broadening. The line-by-line transmission model (Ref. 5) had not been developed at that time. NO concentrations were measured at flight conditions from Mach 1.4 at 35,000 ft to Mach 7.6 at 65,000 ft.

Table 1 shows the results of reducing some of these data by obtaining an average static temperature and static pressure, and using the centerline bandhead transmission to calculate an average NO concentration in ppmv. Table 1 gives the original data (Ref. 1) and the data obtained with use of the improved model and compares them to an average probe value. The sample gas extraction data were obtained in the study with a water-cooled, constant-area, stainless steel probe.

#### **3.2 JET ENGINE COMBUSTOR EXHAUST (REF. 2)**

Reference 2 considers NO emission from a T-56 turbine engine combustor using JP-4 at a constant fuel/air ratio of about 0.013. Pyridene was added to the fuel to increase NO production under certain conditions. Table 1 shows the results of calculating the average NO concentration by the method described previously. The results of the original model (reported in Table 1, AEDC-TR-76-134) and of the corrected model are compared to an average probe value.

The probe measured static temperature and static pressure profiles. Transmission profiles were also used directly in an inversion technique to derive an NO concentration radial profile for the two downstream stations reported. The details of the original inversion

technique and a revised technique are discussed in Refs. 2 and 7, respectively. The original and corrected data for the stations 3 in. and 18 in. downstream are shown in Figs. 4 and 5, respectively. The probe used was an uncooled, constant-area, stainless steel probe.

### **3.3 TURBINE ENGINE COMBUSTOR (REF. 3)**

This report documents the measurement of exhaust product species on a 14.0-cm-diam AVCO Lycoming development turbine engine combustor that was loaned to AEDC. Data were taken at various fuel/air ratios (0.01 to 0.05) at a station 1.27 cm downstream from the combustor nozzle exit. Table 1 shows the results of calculating the average NO concentration. As before, the results of the original model (Table 5, AEDC-TR-76-180) and the corrected model are compared to an average probe value. A water-cooled, constant-area probe was used to obtain the gas sample data reported.

### **3.4 F101-GE-100 TURBOFAN ENGINE (REF. 4)**

This report describes the measurement of pollutant species in the exhaust gases of an F101-GE-100 jet engine. NO and NO<sub>x</sub> absorption data were taken at the intermediate and maximum afterburn power settings. The optical and probe measurements were made at a station 10.2 cm downstream of the nozzle exit of two engines of different serial numbers that had very similar performance characteristics.

Gas sample probe data were obtained at several simulated flight conditions at only the intermediate engine power setting. Comparison between probe and optical results can only be made, then, at this power level. The optical and probe data were not taken at the same altitude, but a probe profile was interpolated from the values corresponding to altitudes which bracketed the optical data acquisition point.

The inversion technique was reapplied to the data reported in Ref. 4 at the intermediate power setting. Figure 6 compares the NO and NO<sub>x</sub> probe profiles to the results of the original inversion technique as reported in Fig. 11 of Ref. 4 and to the results of the inversion technique using the improved model. An orifice probe similar to the "proper design" probes described in Refs. 19 and 20 was used to obtain the gas sample data reported.

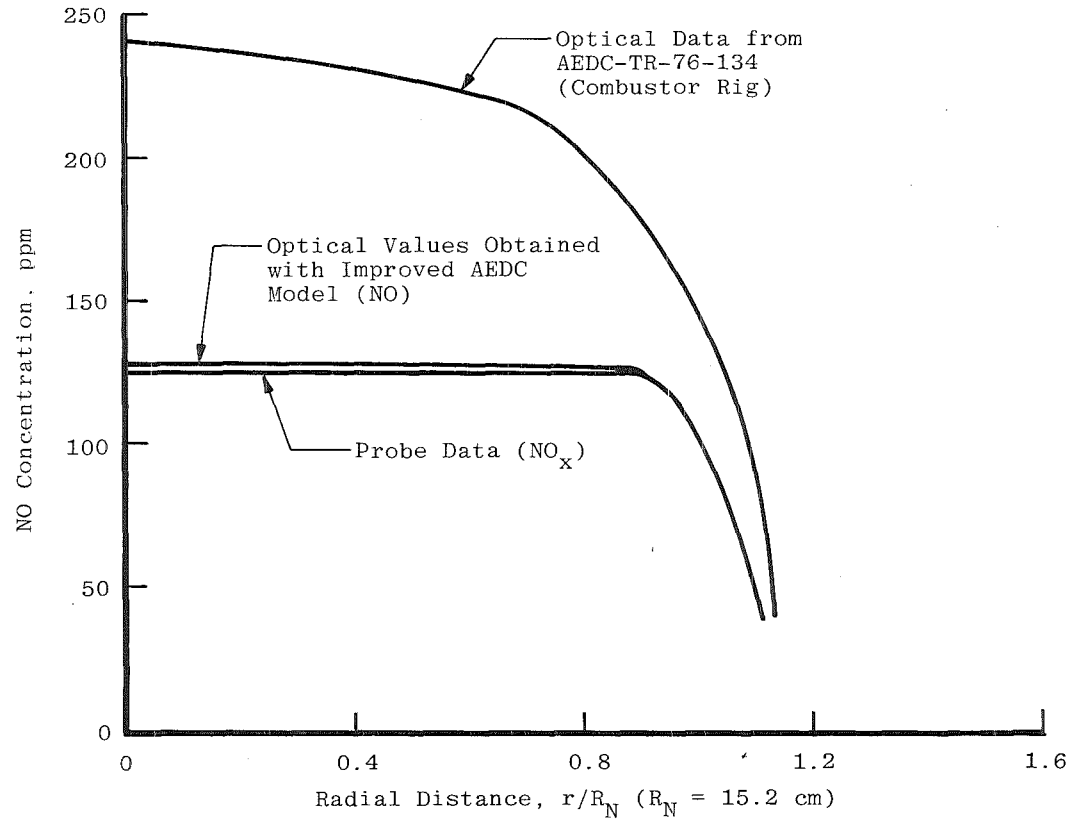


Figure 4. Comparison of the measured probe profiles with the results of the original inversion technique (Fig. 10a of AEDC-TR-76-134) at a station 7.62 cm downstream from combustor exhaust duct exit.

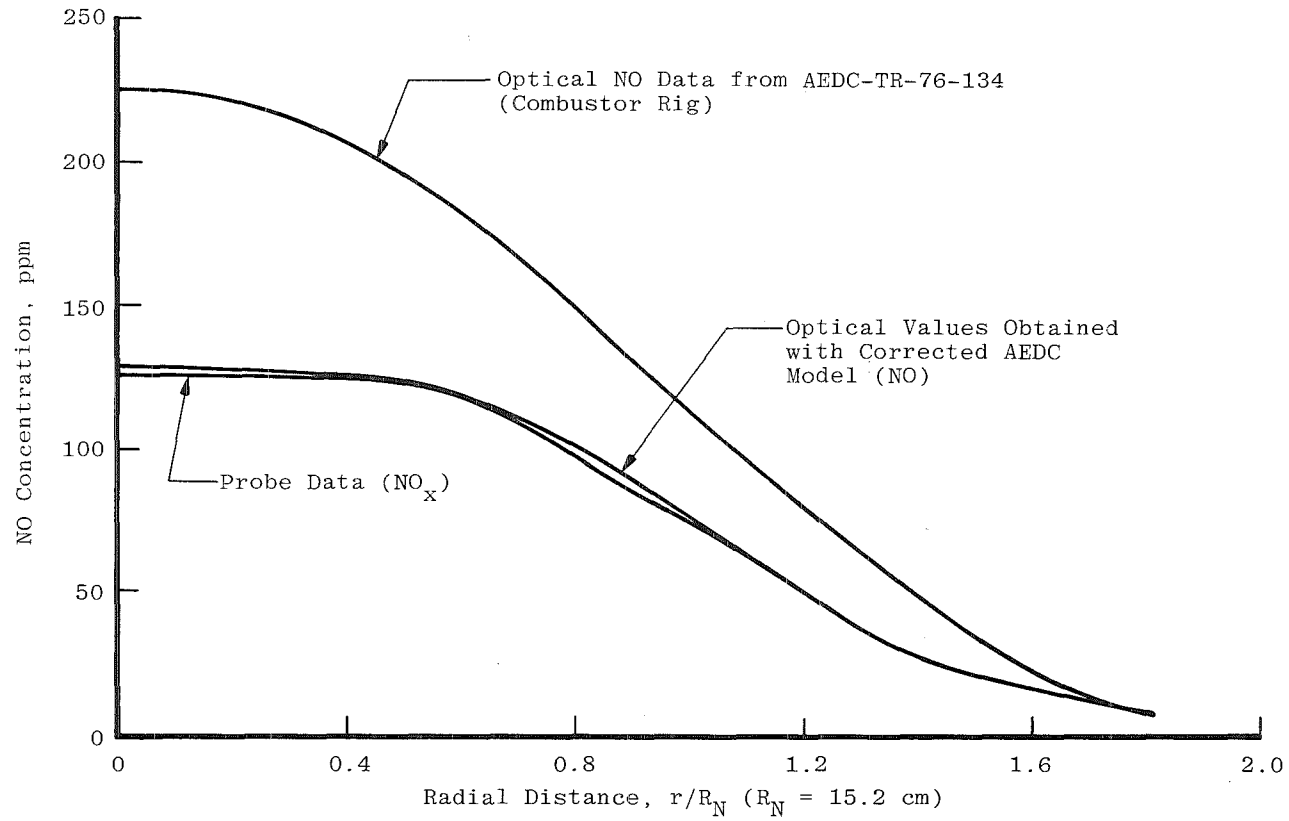


Figure 5. Comparison of the probe profile with results of the original inversion technique (AEDC-TR-76-134) at a station 45.72 cm downstream of combustor exhaust duct exit.

Table 1. Example Results for NO Measurements Made Previously

Condition	Average Static Temperature K	Average Static Pressure, psia	Path Length, cm	Measured Transmissivity, Optical Method	Average NO Conc., Optical, Originally Pub., (ppm)	Average NO Conc., Optical, Improved Model, (ppm)	Ratio of $Opt_{\infty}$ to Probe	Average NO <sub>x</sub> Probe Reported
AEDC-TR-79-132 YJ93-GE-3 Jet Engine								
Alt = 65,000 ft Mach = 2.6 Military Power	506	0.99	112.0	0.626	323	436	4.36	100
Alt = 65,000 ft Mach = 2.6 Max. A/B	868	1.52	127.0	0.594	617	686	5.28	130
AEDC-TR-76-134 WPAFB-T56 Combustor								
7.62 cm Dnst. N.E.*	847	14.7	30.4	0.884	170	119	1.09	109
7.62 cm Dnst. N.E. (Pyridene)	847	14.7	30.4	0.875	190	129	1.03	125
7.62 cm Dnst. N.E. (pyridene)	847	14.7	30.4	0.830	270	181	1.17	154
AEDC-TR-76-180 Avco-Lycoming Combustor All Data Obtained 1.27 cm Downstream of Nozzle Exit								
<u>Fuel-to-Air Ratio:</u>								
0.01	789	20.2	6.0	0.979	175	82	2.73	30
0.02	1,022	15.0	6.0	0.952	605	305	3.0	102
0.03	1,332	17.1	6.0	0.931	860	617	3.25	190
0.04	1,550	16.7	6.0	0.920	1,220	953	4.43	215
0.05	1,724	18.1	6.0	0.910	1,600	1,236	4.68	264

\*Downstream of Nozzle Exit

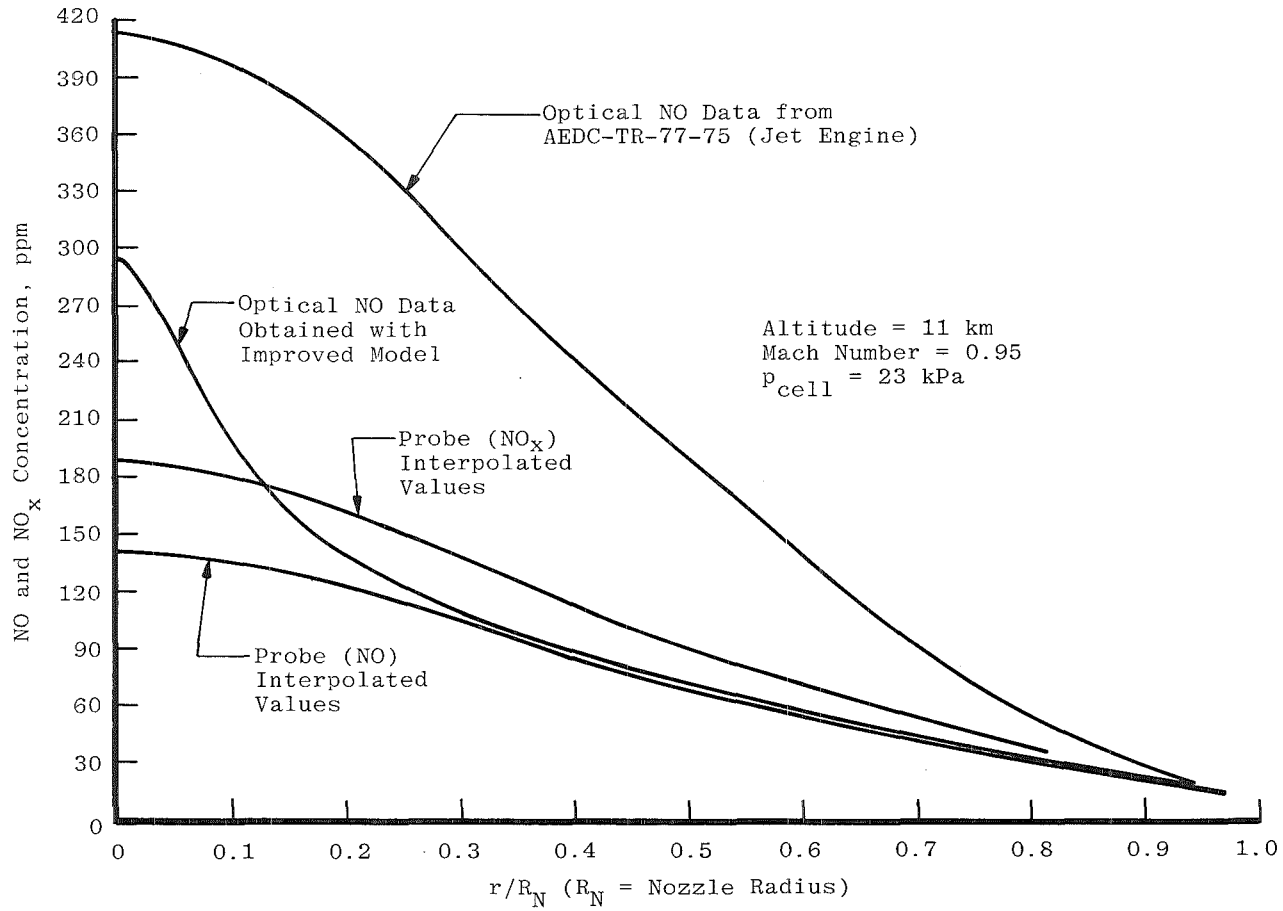


Figure 6. Comparison of the reevaluated NO and NO<sub>x</sub> probe profiles with results of the original and improved model (AEDC-TR-77-75) 10.8 cm downstream of engine nozzle exit.

## 4.0 DISCUSSION

### 4.1 PREVIOUSLY REPORTED DATA

The optically determined NO concentration data reported in the literature have been corrected; the more significant data are presented herein. The data presented here are intended to indicate the magnitude of error in the previously reported results.

1. For the YJ93-GE-3 engine (Ref. 1) two data points give a higher NO concentration than the original results, with a correction for each of about 9 and 46 percent, respectively. The ratio of corrected optically determined values to probe sampling values ranges from 4.4 to 5.3, compared to previously reported values of 3.2 to 4.7. It is important to note that these data are averaged along the path and that the original data were reduced by extrapolation of laboratory measurements rather than by correlation with the radiative transfer computer model.
2. For the T-56 combustor (Ref. 2), all newly determined average NO concentrations are smaller than those previously reported, with an average reduction of about 24 percent. The ratio of corrected optically determined to probe-determined average values ranges from 1.03 to 1.17, probably within the data reproducibility. For the data reduced by the inversion procedure, the corrected NO concentrations at centerline are lower than those originally reported. The corrections are 46 percent at the 3-in. station and 40 percent at the 18-in. station. The optically determined values now agree very well with the probe-determined values.
3. For the Avco-Lycoming combustor, the percent correction in the optically determined values ranges from 22 to 31 percent for the five different fuel-to-air ratios used. The ratio of corrected optical to probe concentrations ranges from 2.7 to 4.6, whereas the range of the originally determined ratios was from 5.8 to 6.0.
4. Using the inversion technique, the percent correction for the centerline value of NO is 27 percent for the F101-GE-100. The ratio of corrected optical to probe NO<sub>x</sub> centerline concentration is 1.52 compared to 2.1 as previously reported. The ratio of corrected optical to probe NO centerline concentration is 2.00.

It is to be noted that the optically determined NO concentration is generally in close agreement with the probe-determined NO<sub>x</sub> concentration for the low-velocity, low fuel-to-air ratio combustion streams encountered from the T-56 combustor rig in which an orifice probe was used. But, for the higher-velocity, higher-temperature reactive plume of the Avco-Lycoming combustor, the optically determined NO concentrations are a factor of 2.4 to 4.7 greater than the probe value where the data are taken only 0.5 in. downstream from the nozzle exit (before any possible mixing can occur) and where a constant-area probe was used. Notice also that the ratio of optical-to-probe values is highest at the highest fuel-to-air ratios and the respective higher temperatures. The jet engine data (NO to NO<sub>x</sub>), also under high-velocity and high-temperature conditions, have relatively high optical-to-probe ratios. For the YJ-93 turbojet engine, the ratio of the average concentration values was about 4 for military power operation; for the F101-GE-100 turbofan engine operating at military power, the centerline ratio was about 1.5 for probe NO<sub>x</sub>, but in the cooler, nonreacting fan region, the optical and probe values agreed quite closely. Thus, it appears that plume mixing and temperature may be extremely important factors in determining the relative differences between the results obtained with the probe and the optical technique. Trends in the probe-measured NO and NO<sub>x</sub> concentrations, however, lead one to conclude that some chemical effects take place within the probe and/or sample line. Different probe designs gave significantly different NO concentrations; therefore, probes must be specially designed for each application (Ref. 20).

## 5.0 CONCLUSIONS

Although errors were found in the original model for transmission of NO  $\gamma$ -band resonance bands through absorbing media, they were partly self-compensating because of the use of the model in determining the line-broadening parameter, which plays a major role in the numerical calculations. Thus, previously published values of NO concentration determined by the optical method in high-velocity and high-temperature streams did not differ greatly from values obtained with the improved model. This was demonstrated by all the cases (both high-velocity and high-temperature) examined, and the previously reported large differences in optical and probe sampling determinations of concentrations in high-velocity, high-temperature flows were sustained. For the case of low-velocity nonreacting flows, the probe and optical results were very nearly the same. Also, in the mixed, fan flow region of a turbofan engine exhaust, the results for the probe and optical techniques agreed.

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NOTE

NOTE OF CORRECTION: BROADENING OF NO  $\gamma$ -BAND LINES†

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**Abstract**—Errors in Ref. 1 are corrected. Using the new data, the collisional broadening coefficient of NO  $\gamma$ -band lines by N<sub>2</sub> is 2390 ( $\pm 220$ ) atm<sup>-1</sup>-K (old value = 1270  $\pm$  200) and the optical collision diameter is 13.3  $\pm$  0.6 Å (instead of 3.5  $\pm$  0.3 Å). Values for argon (2150  $\pm$  200 atm<sup>-1</sup>-K) and CO<sub>2</sub> (2040  $\pm$  200 atm<sup>-1</sup>-K) yield the optical collision diameters of 13.2 and 13.1 Å, respectively.

INTRODUCTION

Some of us previously<sup>1</sup> determined broadening parameters in electronic transition bands of diatomic molecules. Dodge and Dusek<sup>2</sup> have found that our expressions for the ground state partition function for NO and the normalization of the oscillator strength values were inconsistent with some published work<sup>3</sup> and also identified minor errors in the computer program. We have reexamined and corrected the theory, made more precise laboratory measurements, and redetermined the broadening parameter for the  $\gamma$ -bands of NO.

REVISION OF MODEL

The X<sup>2</sup>Π state of the NO molecule belongs to the coupling case intermediate between Hund's cases (a) and (b)<sup>4</sup> for which the rotational energy levels may be calculated approximately from Ref. 5 while the rotational line strength (Hönl-London) factors follow the Earls formula<sup>6</sup> normalized according to Tatum.<sup>7</sup> In the original paper<sup>1</sup>, Hund's case (b) statistics were erroneously applied. The population density of quantum level  $v$ ,  $J$ , spin sub-level  $c$ , and parity  $p$  is for the intermediate coupling case

$$N(v'', J'', c, p) = \frac{N_{\text{total}}(2J'' + 1) \exp\{-[G(v'') + F_c(J'')]/\kappa T\}}{2 \sum_p \{ \exp[-G(v'')/\kappa T] \sum_{c=1}^{\infty} \sum_{J''=0}^{\infty} (2J'' + 1) \exp[-F_c(J'')/\kappa T] \}} \quad (1)$$

where  $G(v'')$  is the vibrational energy,  $T$  is the temperature,  $\kappa$  is Boltzmann's constant, and  $F_c(J'')$  is the rotational energy given approximately by the Hill and van Vleck formulae.<sup>5</sup> Equation (1) yields values of  $N_{v'', J'', c, p}$  approximately half as large as Eq. (8) of Ref. 1.

Equation (9) of Ref. 1 does not comply with the normalization in Ref. 3 which was used for the band oscillator strength  $f_{v'' J'' K'' v' J' K'}$ ; the correct expression for the line oscillator strength  $f_{v'' J'' K'' v' J' K'}$  is

$$f_{v'' J'' K'' v' J' K'} = f_{v'' v'} \frac{\nu_{J'' K'' J' K'}}{\nu_{v'' v'}} \frac{S_{J'' K'' J' K'}}{2J'' + 1} \quad (2)$$

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where  $\nu_{JKJK}$  and  $\nu_{\gamma}$  are the frequencies of the line and band centers, respectively, and  $S_{JKJK}$  is the Hönl-London factor. We prefer the most recently reported<sup>8</sup> value  $4.09 \pm 0.1 \times 10^{-4}$  for the band oscillator strength of the 0,0 band of the NO  $\gamma$ -system in place of  $3.64 \pm 0.05 \times 10^{-4}$ .

When Eqs. (1) and (2) are used, Eq. (7) of Ref. 1 becomes

$$k_{\nu}^{\circ} = \frac{2e^2 \sqrt{\pi \ln 2} N(v'' J'' cp) f_{eJKJK}}{mc^2 (\Delta_{\nu})_D} \quad (3)$$

where  $e$  and  $m$  are the electronic charge and mass,  $c$  is the speed of light and  $(\Delta_{\nu})_D$  is the Doppler line width. The computer model was reconstructed using Eqs. (1)–(3). Also, the improved line locations of Engleman, Rouse, and Baramonte<sup>9</sup> were used rather than those of Deezi,<sup>10</sup> as suggested by Dodge and Dusek.<sup>2</sup>

#### EXPERIMENTAL DATA

Many experimental data were obtained using the apparatus of Ref. 1. We now believe that some of the NO densities reported in Ref. 1 were in error because of interactions of NO with the Hg in the McLeod gauge.

The effective temperature of the source was measured in the current work rather than assumed. In the limit of zero partial pressure of broadening gas and with a small absorber pressure ( $\sim 10^{-3}$  atm), the absorber line shape reduces to a Doppler profile, and the transmissivity of a narrow line source depends only upon the source line width. The measured transmissivity was extrapolated to zero broadening gas pressure (see Fig. 1). The source temperature in the model was adjusted until the transmissivity at zero broadening gas pressure agreed with the extrapolated measured value. The result was  $950 (\pm 25)^{\circ}\text{K}$ .

Values of the Voigt line profile parameter  $a'$  required to match measured and calculated transmissivities at the 2nd bandhead of the 0,0  $\gamma$ -band were plotted vs  $P/T$ , and the slope was determined for either  $\text{N}_2$ , Ar, or  $\text{CO}_2$  as the foreign gas. Results for  $\text{N}_2$  are shown on Fig. 2 and

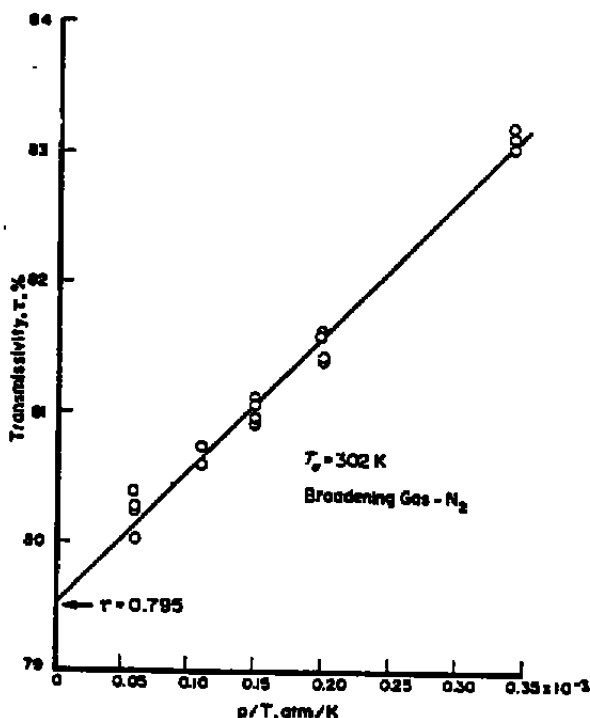


Fig. 1. Least-squares fit to the transmissivity at the first bandhead of the 0,0 NO  $\gamma$ -band vs  $P/T$  in the limit as the pressure goes to zero.

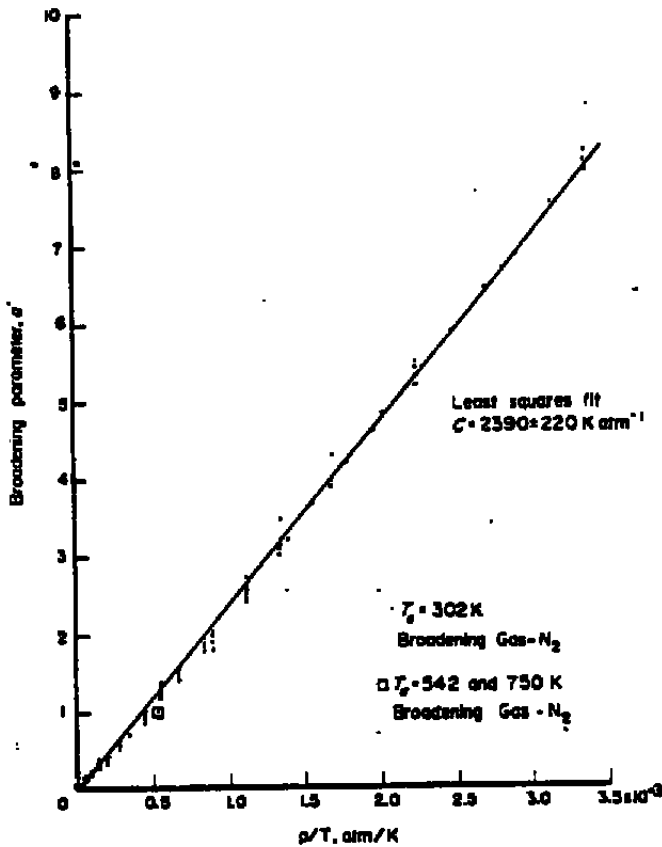


Fig. 2. Values of the spectral broadening parameter ( $a'$ ) as a function of  $p/T$  for the (0, 0)  $\gamma$ -band of NO.

broadening coefficients obtained are given as follows:

$$\begin{aligned}
 a' &= C P/T \\
 \text{for } \text{N}_2, \quad a' &= (2390 \pm 220) P/T; \\
 \text{for } \text{Ar}, \quad a' &= (2150 \pm 200) P/T; \\
 \text{for } \text{CO}_2, \quad a' &= (2090 \pm 200) P/T;
 \end{aligned}
 \tag{4}$$

here the value of  $C$  has the units  $\text{atm}^{-1}\text{-K}$ .  
 For bimolecular broadening collisions,<sup>11</sup>

$$C = \frac{\lambda P_0}{\pi^{1/2} \kappa} \left( 1 + \frac{M_a}{M_b} \right)^{1/2} \sigma_{ab}
 \tag{5}$$

where  $\sigma_{ab}$  is the collisional cross section for broadening of the absorbing molecules  $a$  by molecules of species  $b$ ,  $\lambda$  is the wavelength,  $P_0$  is atmospheric pressure at standard conditions,  $\kappa$  is Boltzmann's constant,  $M_a$  is the mass of the primary molecule, and  $M_b$  is the mass of the foreign broadening molecule. Thus, for the NO  $\gamma$ -band, we obtain the data listed below.

Broadening gas	Cross section ( $10^{-16} \text{ cm}^2$ )	Optical collision diameter ( $\text{\AA}$ )
$\text{N}_2$	$556 \pm 53$	$13.3 \pm 0.6$
$\text{Ar}$	$547 \pm 53$	$13.2 \pm 0.6$
$\text{CO}_2$	$540 \pm 53$	$13.1 \pm 0.6$

In our original paper, the exponent of the constant in Eq. (11) was incorrect; it should have been  $10^{18}$  and not  $10^{19}$ . The result was an error in the reported optical collisional diameter; it should have been 11 Å and not 3.5 Å. The values of the collisional diameter ( $d_{ab}$ , defined by  $\sigma_{ab} = \pi d_{ab}^2$ ) reported here are about 13 Å and are in substantial disagreement with that of Thorsen and Badger.<sup>12</sup>

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