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STUDIES OF RADIANT HEAT TRANSFER

FROM PURE GASES

Thesis by

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ABSTRACT

This report contains an outline of some of the experimental measurements and theoretical considerations which are required for the calculation of the emissivity of nitric oxide. Because of lack of suitable apparatus, the experimental part of the program was restricted to the determination of apparent absorption coefficients for the fundamental vibration-rotation band of nitric oxide. Theoretical calculations of emissivity were originally suggested by Dr. Martin Summerfield. The present calculations were made by the use of an approximate procedure which has been developed recently at the Jet Propulsion Laboratory by S. S. Penner for the determination of the emissivity of pure diatomic gases. The results presented in this report facilitate making approximate estimates of the emissivity of nitric oxide as a function of temperature and optical density. For these emissivity calculations it is recommended to correct the experimentally determined apparent absorption coefficients by analogy with available data for carbon monoxide.

TABLE OF CONTENTS

RADIANT HEAT TRANSFER FROM PURE GASES

I. INTRODUCTION AND SUMMARY

Recent development of propulsive systems and propellants capable
of taxing the heat resisting properties of our best alloys has aroused
considerable interest in the field of heat transfer. While this in-
terest has led to extensive research within the broader limits of this
field, the theoretical treatment of radiant heat transfer has received
relatively little attention.

Theoretical studies of radiant heat transfer are based on Ein-
stein's work on transition coefficients[1]. More recent contributions
from the fundamental point of view have been made by Born[2], Slater[3],
and Dirac[4]. As a result of this work it is now possible, in principle,
to make radiant heat transfer calculations. However, the complexity of
these calculations is such that they are scarcely adaptable to the nu-
merical calculation of emissivities for practical applications.

Because of the difficulties involved in the theoretical calcula-
tions of radiant heat transfer, it has been customary to collect empir-
ical emissivity data as a function of pressure, temperature, and path
length[5]. By using available emissivity data many problems on radiant
heat transfer involving relatively low temperatures are now capable of
approximate solution. However, since the emissivities of only a limited
number of gases are known, and since, furthermore, the temperature and

pressure extrapolation of available data is not possible with a high
degree of accuracy, the empirical method has a rather limited range
of application.

It is apparent from the foregoing considerations that a more
fundamental approach to the practical problem of radiant heat trans-
fer is highly desirable, especially for the purpose of calculating
the temperature dependence of the emissivity. As the first step of
a broad program on the study of radiant heat transfer now being con-
ducted at the Jet Propulsion Laboratory, an approximate method[6] has
been developed for the calculation of average emissivities of dia-
tomic gases as a function of temperature and optical density. The
present report will be devoted to the application of this method to
the determination of the emissivities of nitric oxide as a function
of temperature, pressure, and path length. The report is completed
by a description of apparent absorption coefficient measurements of
nitric oxide performed on a Model 12-C Perkin-Elmer spectrometer using
a lithium-fluoride prism.

II. FUNDAMENTAL RELATIONS OF RADIANT HEAT TRANSFER

This section will be devoted to a description of some of the important basic equations of radiant heat transfer and to a discussion of the relations between line strengths, Einstein coefficients, and spectral emissivities. These equations are, of course, well known but are summarized here in order to clarify the numerical calculations of emissivities described in Section IV.

According to Beer's law for the absorption of radiation by an isotropic substance, the transmitted intensity varies exponentially according to the relation

$$I_\nu = I_{o\nu}\, e^{-P_\nu\, p\, l} \tag{1}$$

where I_ν is the intensity of the transmitted light in the spectral region between ν and $\nu + d\nu$, $I_{o\nu}$ is the intensity of the incident light in the same spectral range, P_ν is the true spectral absorption coefficient of the absorber, and the product of the pressure $\underline{p}$ and the path length $\underline{l}$ is the optical density of the absorber. The intensity of the light absorbed is, therefore,

$$A_\nu = I_{o\nu} - I_\nu = I_{o\nu}(1 - e^{-P_\nu\, p\, l}). \tag{2}$$

According to Kirchhoff's law the ratio of the spectral emissivity to the spectral absorptivity is unity for all substances. The absorptivity is defined as the fraction of the incident light absorbed and the emissivity as the ratio of the intensity of the light emitted by

a given substance at temperature T to that emitted by a blackbody
at the same temperature. For an isotropic gaseous emitter, the spec-
tral emissivity, $\mathcal{E}_\nu$, is, therefore, given by the relation

$$\mathcal{E}_\nu = 1 - e^{-P_\nu p \, l} \, . \tag{3}$$

The emissivity can be determined experimentally by direct measurement
or by measuring the transmission ratios at various temperatures and
pressures. Since it is difficult to make accurate measurements of this
type over a wide range of temperatures and pressures, it is desirable
to consider theoretically the temperature and pressure dependence of P_ν.

According to the Bohr frequency rule, transition between two non-
degenerate, stationary energy states of values E_i and E_j with $E_i > E_j$
will be accompanied by the emission of radiant energy of the frequency

$$\nu_{ij} = \frac{E_i - E_j}{h} \, . \tag{4}$$

where h is Planck's constant.

For radiation emitted from an oscillating dipole, if the time be-
tween collisions is large compared to the duration of a collision, it
can be shown[7] that the spectral absorption coefficient is related to
the line strength, $\int_{-\infty}^{+\infty} P\nu_{ij} d\nu_{ij}$, and the spectral-line half-width, δ_{ij},
by the well-known dispersion formula of Lorentz,

$$P_\nu = \frac{\frac{\delta_{ij}}{\pi} \int_{-\infty}^{+\infty} P\nu_{ij} d\nu_{ij}}{(\nu - \nu_{ij})^2 + \delta^2_{ij}} \, . \tag{5}$$

The spectral-line half-width is defined as the frequency interval for
which absorption is greater than one-half the maximum absorption.

Reference to equation (5) indicates that the absorption coefficient can be calculated if the line strength and the line shape are known. Although the spectral half-width is a function of temperature and pressure, this dependence will not be discussed in this report, since it is desired to present an approximate method for radiant heat transfer calculations in which no explicit allowance is made for the change of δ_{ij} with pressure and temperature. Since the line strength is independent of pressure[8], it remains only to discuss its temperature dependence in order to determine P_ν as a function of temperature. Theoretical calculations of $\int_{-\infty}^{+\infty} P_\nu \, d\nu$ as a function of temperature require the use of relations which can be derived from the Einstein coefficients of absorption and emission[9]. These relations will now be discussed.

The probability that a molecule will absorb a quantum of energy and undergo a transition to a higher energy level in a blackbody radiation field is given by the term $B_{j \to i} \rho(\nu_{ij})$ where $B_{j \to i}$ is the Einstein transition coefficient of induced absorption and $\rho(\nu_{ij})$ is the density of radiation emitted by a blackbody between frequencies ν_{ij} and $\nu_{ij} + d\nu_{ij}$. The probability of transition from an upper to a lower energy level is, on the other hand, the sum of two parts, one being independent and the other proportional to the radiation density, i.e.:

$$A_{i \to j} + B_{i \to j} \rho(\nu_{ij})$$

where $B_{i \to j}$ and $A_{i \to j}$ are the Einstein coefficients of induced and spontaneous emission, respectively. At thermal equilibrium the net rate of transition is zero, and, therefore,

$$N_i A_{i \to j} = (N_j B_{j \to i} - N_i B_{i \to j}) \rho(\nu_{ij})$$

where N_i and N_j are the number of molecules in the i'th and j'th energy levels. Noting that the net energy absorbed is

$$E_a = (N_j B_{j \to i} - N_i B_{i \to j}) h \nu_{ij} \rho(\nu_{ij}) \tag{6}$$

and defining the spectral line strength in absorption[10] by the relation

$$E_a = c \rho(\nu_{ij}) \int_{-\infty}^{+\infty} P \nu_{ij} \, d\nu_{ij} \tag{7}$$

where c is the velocity of light, it follows that

$$\int_{-\infty}^{+\infty} P \nu_{ij} \, d\nu_{ij} = N_i A_{i \to j} h \nu_{ij} / c \rho(\nu_{ij}) \tag{8}$$

Equation (8) is the fundamental relation between line strength in absorption and the Einstein coefficient of spontaneous emission.

The net rate at which molecules jump from the upper to the lower energy level is assumed to be given by an expression of the form[10]

$$N_i \left[A_{i \to j} + B_{i \to j} \rho'(\nu_{ij}) \right] - N_j B_{j \to i} \rho'(\nu_{ij}) \tag{9}$$

where $\rho'(\nu_{ij})$ is the external radiation density. Hence for $\rho'(\nu_{ij})$ vanishingly small the emitted radiant intensity is

$$\int_{-\infty}^{+\infty} I \nu_{ij} \, d\nu_{ij} = N_i A_{i \to j} h \nu_{ij} \tag{10}$$

which defines the line strength in emission $\int_{-\infty}^{+\infty} I_{\nu_{ij}} d\nu_{ij}$, for an $i \to j$ transition. From equations (8) and (10) it can be seen that

$$\int_{-\infty}^{+\infty} I_{\nu_{ij}} d\nu_{ij} = c\rho(\nu_{ij}) \int_{-\infty}^{+\infty} P_{\nu_{ij}} d\nu_{ij} \tag{11}$$

which is equivalent to Kirchhoff's law.

For a transition between the adjacent vibrational levels n-1 and n the line strength in absorption is given, approximately, by the following relation

$$\int_{n-1 \to n} P_\nu \, d\nu = \frac{h\nu_o}{c\rho(\nu_o)} N_n A_{n \to n-1} \tag{12}$$

where

$$\int_{n-1 \to n} P_\nu \, d\nu = \sum_j \left\{ \int_{\substack{n-1 \to n \\ j \to j-1}} P_\nu \, d\nu + \int_{\substack{n-1 \to n \\ j-1 \to j}} P_\nu \, d\nu + \int_{\substack{n-1 \to n \\ j \to j}} P_\nu \, d\nu \right\}^* , \tag{13}$$

and

$$A_{n \to n-1} = \sum_j \left\{ A_{\substack{n \to n-1 \\ j \to j-1}} + A_{\substack{n \to n-1 \\ j-1 \to j}} + A_{\substack{n \to n-1 \\ j \to j}} \right\} . \tag{14}$$

Equation (12) involves the approximation of replacing the different frequencies corresponding to different vibration-rotation transitions by an average value, ν_o, which, as a good approximation, may be set equal to the frequency difference corresponding to the vibrational transition $n = 0 \to n = 1$ and the rotational transition $j = 0 \to j = 0$.

The use of Planck's law of radiation, of Boltzmann's equation for the population of molecules in different vibrational levels under

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*It should be noted that NO has a permanent electric moment in the direction of the internuclear axis, and that, therefore, its infrared vibration-rotation spectrum shows P, Q, and R branches.

equilibrium conditions, and of Bohr's correspondence principle permits
the derivation of the following relation[6, 11, 12]

$$\int_{n-1 \to n} P_\nu \, d\nu \approx \frac{N_T \pi \mathcal{E}^2}{3 \mu c} \left\{ 1 - e^{-\frac{h\nu_o}{kT}} \right\} \frac{n \, e^{-(n-1)\frac{h\nu_o}{kT}}}{\sum_{n=1}^{\infty} e^{-(n-1) h\nu_o / kT}}$$

or

(15)

$$\sum_{n=0}^{\infty} \int_{n-1 \to n} P_\nu \, d\nu \approx \frac{N_T \pi \mathcal{E}^2}{3 \mu c}$$

where N_T is the total number of molecules, $\mathcal{E}$ is the effective charge,
and μ is the reduced mass of the molecule. Equation (15) states that
the summation of the line strengths contributing to emission or absorp-
tion in the region of the fundamental vibration-rotation band is inde-
pendent of the temperature for a given number of emitters. This relation
will be used in the approximate calculation of emissivities described in
Section IV.

III. ABSORPTION COEFFICIENTS

A. INTRODUCTION

This section is devoted to a discussion of true, apparent, and average absorption coefficients. The introduction includes a brief description of the methods used by Bourgin[13] and Bartholome'[14] for the determination of true absorption coefficients. Because of lack of suitable equipment for the determination of the true absorption coefficients, the experimental studies were restricted to the measurement of apparent absorption coefficients. The significance, use, and temperature dependence of an apparent average absorption coefficient will also be considered.

The method used by Bourgin does not permit the determination of true absorption coefficients directly, but does allow the calculation of spectral line-strengths. Once spectral line-strengths have been obtained it is possible to calculate true absorption coefficients by application of the Lorentz dispersion formula (Cf. Eq. 5) provided half-width data have also been obtained. The general plan used by Bourgin for determining line intensities involves the accurate measurement of the area under each absorption line for several cell lengths, the pressure being maintained constant.* Because the instrument available for the present experiment did not give sufficiently high resolution, Bourgin's method could not be used. If a plot is made of percentage of light absorbed against wave number, it follows that the area A_M, under the absorption line M is given by the expression

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*It is evident that this technique requires high spectral resolution in order to separate the rotational fine structure of the absorption band.

$$A_M = \int_M \left[1 - \frac{I_\nu}{I_{o\nu}} \right] d\nu \tag{16}$$

Expanding the exponential term in Beer's law for sufficiently small
values of the optical density, p., leads to the relation

$$\frac{I_\nu}{I_{o\nu}} \simeq 1 - P_\nu \, pl \tag{17}$$

Combining equations (16) and (17) yields the result that

$$A_M = pl \int_M P_\nu \, d\nu \tag{18}$$

From equation (13) it then follows that

$$\lim_{pl \to 0} \frac{d \, A_M}{dpl} = \int_M P_\nu \, d\nu \tag{19}$$

i.e., the integrated absorption coefficient, or the line strength, is
equal to the slope of an area versus length plot for the limiting case
of zero cell length. In order to permit accurate extrapolation of
this curve to zero, small cell lengths were employed. It should be
mentioned that the extrapolation of the curve to the zero value of the
optical density becomes a difficult problem because of the rapid change
of slope of the curve at small values of pl.

Bartholomé's method has the advantage over Bourgin's of not re-
quiring high resolution. By the introduction in the light absorption
cell of another gas which is optically inactive in the infrared region
of study, the total pressure is increased to the point where the

rotational lines overlap sufficiently to obliterate completely the
fine structure. This method is now being employed at the Jet Propulsion
Laboratory to determine the relation between the true absorption coef-
ficient and an absorption coefficient measured with low resolution and
at low pressures, i.e., an apparent absorption coefficient.

Before proceeding to discuss the apparent absorption coefficient,
it is of interest to note that an approximate method is available for
the determination of an average value of the line strength for a given
absorption band. This method was originally proposed by Dennison[15]
and has been modified by Cornell[16], Elsasser[17], Summerfield[18],
and others. The principal objection to this method is the necessity
for assuming that the rotational lines are of equal intensity and are
equally spaced. In spite of the fact that these assumptions are invalid
for real molecules, it should be pointed out that the method of Elsasser
and Summerfield has been shown to lead to reasonable numerical
results[17, 18].

B. EXPERIMENTAL RESULTS

The apparent absorption coefficient, P_ν', is a coefficient replac-
ing the true absorption coefficient, P_ν, in Beer's law and is determined
with resolution insufficient to study individual rotational lines and
at pressures lower than required to give complete overlapping of the
rotational lines. Since the necessary facilities for carrying out an
accurate determination of the true line strength were not available at
the time the studies described in this thesis were conducted, it was
decided to measure apparent absorption coefficients with the infrared

spectrometer available to the author. It is recognized that the
relation between true and apparent coefficients is unknown. However,
the preliminary measurements of apparent coefficients described in
this thesis should be of value ultimately to the overall program of
heat transfer now under way at the Jet Propulsion Laboratory. By use
of the empirically determined relations between true and apparent
coefficients for CO, the values of the apparent coefficients of NO
can be converted approximately to the true values. That the true and
apparent absorption coefficients for CO and NO should be related fol-
lows from the similarity in rotational spacing and resolution in the
P and R branches of the fundamental absorption bands of these two com-
pounds. The apparent absorption coefficients were determined by straight-
forward application of Beer's law. From the linearized form of this law,
it can be seen that

$$\ln \frac{I_\nu}{I_{o\nu}} = - P_\nu' \, pl \tag{20}$$

where P_ν' is, in general, a function of pressure. In the limiting
case of zero optical density, pl, it can be seen that

$$P_\nu' = - \lim_{pl \to 0} d\left[\ln (I_\nu/I_{o\nu})\right] / d(pl) \tag{21}$$

Since the path length was kept constant because cells of different lengths
were not available, equation (21) may be written as

$$P_\nu' = - \frac{1}{l} \lim_{p \to 0} d\left[\ln (I_\nu/I_{o\nu})\right] / dp \tag{22}$$

from which it follows that the apparent absorption coefficient is

proportional to the limiting slope, for zero pressure, of a plot of
the logarithm of the fraction of the light transmitted as a function
of pressure. In the present investigations the pressure of the absorber
was kept below 1 atmosphere in order to permit more accurate extrapola-
tion of the curve to zero pressure. Readings were made at pressures of
NO corresponding to 13.5, 15.9, 28.3, 36.5, 48.0, 71.6, and 72.0 cm.
of Hg.

All measurements were made on a Model 12C, Perkin-Elmer infrared
spectrometer using a lithium fluoride prism and a 10 cm. long gas cell
closed with sodium chloride windows. A resolution of about 4 wave
numbers was obtained near the center of Q-branch for the fundamental
vibration-rotation band of NO with the particular slit widths employed
for the present studies. The wave length scale had been previously
calibrated by using known absorption lines of H_2O, CO_2, CH_4, and NH_3.
A wave length-micrometer scale reading calibration curve obtained by the
author is shown in figure (1).

Prior to taking transmission readings on the infrared spectrometer,
the instrument was allowed the customary warm-up period of one-half hour
in order to insure stable operation. Next a transmission record was
obtained for the empty gas cell. Then a transmission record was ob-
tained for the cell filled with the gas under the study, and finally
another reference run with the evacuated cell was completed. From
these three sets of data it is possible to obtain reasonably reliable
percentage of transmission values as a function of wave length. The
wave length calibration curve was checked daily by using the water

bands at 1794, 1830, 1846, 1870, 1891, and 1944 cm^{-1} as reference

points. The wave length calibration led to a value for the wave number

at the peak of the ς-branch of 1877.9 cm^{-1} which agrees reasonably well

with results reported by other investigators[19, 20, 21].

Representative data of the logarithm of the percentage of trans-

mission as a function of pressure, calculated from the experimental

measurements are shown in figures (2) and (3). The values of the appar-

ent absorption coefficient computed from these plots are summarized in

Table I and are plotted in figure (4) as a function of the wave number.

TABLE I

APPARENT ABSORPTION COEFFICIENTS FOR NO.

ν cm^{-1}	P_{ν}' (meter-atm)$^{-1}$
1800.0	1.38
1816.5	3.05
1850.8	6.33
1866.4	7.11
1877.9	11.28
1881.8	2.58
1896.8	7.05
1907.7	9.00
1917.0	9.20
1924.0	8.58
1936.1	6.85
1954.0	2.00

C. CALCULATION OF APPROXIMATE AVERAGE ABSORPTION COEFFICIENTS.

From the discussion in Section II it is apparent that rigorous

calculation of spectral emissivities at various temperatures is a pro-

ject of tremendous proportions. In order to avoid some of the

difficulties of radiant heat transfer calculations it was proposed by
Schack[22] to use an absorption coefficient which is a linear function
of the wave number for a given absorption band. Schack used available
experimental measurements for the apparent absorption coefficient, a
procedure which is certainly not justified.

The procedure of Schack for making emissivity calculations can
be further simplified if average absorption coefficients for entire
absorption bands are used. It is clear that if, as a first approxima-
tion, it is possible to use such average coefficients, then the average
coefficients are defined in terms of the effective emissivity by the
relation

$$\varepsilon' = (1 - e^{-\bar{k}_F\, pl}) \frac{\displaystyle\int_{\lambda min}^{\lambda max} I_\lambda\, d\lambda}{\displaystyle\int_0^{+\infty} I_{o\lambda}\, d\lambda} + (1 - e^{-\bar{k}_{F.O.}\, pl}) \frac{\displaystyle\int_{\lambda' min}^{\lambda' max} I_\lambda\, d\lambda}{\displaystyle\int_0^{+\infty} I_{o\lambda}\, d\lambda} + \dots \quad (23)$$

where ε' — effective emissivity

$\bar{k}_F$ — average absorption coefficient for the fundamental band

$\bar{k}_{F.O.}$ — average absorption coefficient for the first overtone

λmax — long wave length cut-off for fundamental.

λmin — short wave length cut-off for fundamental

λ'_{max} — long wave length cut-off for first overtone

λ'_{min} — short wave length cut-off for first overtone

The effective band width of the fundamental is $\lambda_{max} - \lambda_{min}$, and for the
first overtone it is $\lambda'_{max} - \lambda'_{min}$. The effective band width may be

looked upon as the wave length interval over which absorption is of consequence according to a prearranged standard. By comparison of equation (23) with the following relation, which can be derived from equation (2),

$$\sum_n \sum_j \int_{\substack{n\to n+1 \\ j\to j-1}} E_\nu \, d\nu + \sum_n \sum_j \int_{\substack{n\to n+1 \\ j-1\to j}} E_\nu \, d\nu + \sum_n \sum_j \int_{\substack{n\to n+1 \\ j\to j}} E_\nu \, d\nu =$$

$$c \sum_n \sum_j \int_{\substack{n\to n+1 \\ j\to j-1}} \alpha(\nu) \, (1 - e^{-P_\nu \, pl}) \, d\nu + c \sum_n \sum_j \int_{\substack{n\to n+1 \\ j-1\to j}} \rho(\nu)(1 - e^{-P_\mu pl}) \, d\nu +$$

$$c \sum_n \sum_j \int_{\substack{n\to n+1 \\ j\to j}} \rho(\nu) \, (1 - e^{-P_\nu \, pl}) \, d\nu \qquad (24)$$

it can be shown [6] that the average coefficients, if they exist, are of the form

$$\bar{k}_F = \frac{1}{\Delta\nu_F} \sum_n \sum_j \left\{ \int_{\substack{n\to n+1 \\ j-1\to j}} P_\nu \, d\nu + \int_{\substack{n\to n+1 \\ j\to j-1}} P_\nu \, d\nu + \int_{\substack{n\to n+1 \\ j\to j}} P_\nu \, d\nu \right\} \qquad (25)$$

$$\bar{k}_{F.O.} = \frac{1}{\Delta\nu_{F.O.}} \sum_n \sum_j \left\{ \int_{\substack{n\to n+2 \\ j\to j-1}} P_\nu \, d\nu + \int_{\substack{n\to n+2 \\ j-1\to j}} P_\nu \, d\nu + \int_{\substack{n\to n+2 \\ j\to j}} P_\nu \, d\nu \right\} \qquad (26)$$

Here, $\int_{\substack{n \to n+1 \\ j \to j-1}} E_\nu\, d\nu$ represents, for example, the intensity of radiation

absorbed as the result of the transition $n \to n+1$, $j \to j-1$, and $\Delta\nu_F$ and $\Delta\nu_{F.O.}$ are the effective band widths of the fundamental and first overtone, respectively.

Relations of the form of equations (25) and (25a) permit the calculation of average absorption coefficients if the sum of the _true_ line strengths is known. As has been pointed out previously, the present experiments yielded only apparent absorption coefficients. Nevertheless, it is instructive to consider the relations between apparent spectral absorption coefficients and apparent average absorption coefficients. In order to distinguish apparent average coefficients from the true average coefficients, the former will be designated by $\bar{k}'_F$, $\bar{k}'_{F.O.}$, etc. The experimentally observed result that for small values of the optical density, the average apparent absorption coefficient, defined by the relation

$$\int_{\Delta\nu_F} A_\nu\, d\nu = \left\{1 - e^{-\bar{k}'_F p l}\right\} \int_{\Delta\nu_F} I_{0\nu}\, d\nu \tag{26}$$

is identical with the average apparent absorption coefficient

$$\bar{k}'_F = \frac{\int_{\Delta\nu_F} k_\nu'\, d\nu}{\Delta\nu_F} \tag{27}$$

will now be established on the basis of a more detailed analysis of

equation (26).

In the limiting case of small pl, the exponential term in equation (26) can be expanded and only the first two terms retained with the result

$$\int_{\Delta\nu_F} A_\nu \, d\nu \Big/ \int_{\Delta\nu_F} I_{o\nu} \, d\nu = \bar{k}'_F \, pl \qquad (28)$$

from which it follows that for constant path length, l,

$$\frac{1}{l} \frac{d}{dp} \left\{ \frac{\displaystyle\int_{\Delta\nu_F} A_\nu \, d\nu}{\displaystyle\int_{\Delta\nu_F} I_{o\nu} \, d\nu} \right\} = \bar{k}'_F \qquad (29)$$

Furthermore, integration of the spectral form of Beer's Law for the apparent coefficient, P_ν', and for small values of P_ν' pl,

$$\left(1 - \frac{I_\nu}{I_{o\nu}}\right) = P_\nu' \, pl, \qquad (30)$$

yields the result that

$$\int_{\Delta\nu_F} \frac{(I_{o\nu} - I_\nu) \, d\nu}{I_{o\nu}} = pl \int_{\Delta\nu_F} P_\nu' \, d\nu \qquad (31)$$

If the energy of the incident light is nearly independent of frequency within the limits of the effective band width, then equation (31) can

be replaced, approximately, by the relation

$$\frac{\displaystyle\int_{\Delta\nu_F}(I_{o\nu}-I_\nu)\,d\nu}{\displaystyle\int_{\Delta\nu_F}I_{o\nu}\,d\nu} = \frac{\displaystyle\int_{\Delta\nu_F}A_\nu\,d\nu}{\displaystyle\int_{\Delta\nu_F}I_{o\nu}\,d\nu} = \frac{p\,1}{\Delta\nu_F}\int_{\Delta\nu_F}P'_\nu\,d\nu$$

and, therefore,

$$\frac{1}{\ell}\frac{d}{dp}\left\{\frac{\displaystyle\int_{\Delta\nu_F}A_\nu\,d\nu}{\displaystyle\int_{\Delta\nu_F}I_{o\nu}\,d\nu}\right\} = \frac{\displaystyle\int_{\Delta\nu_F}P'_\nu\,d\nu}{\Delta\nu_F} \tag{32}$$

Comparison of equations (29) and (32) leads to the desired result

$$\bar{k}'_F = \frac{\displaystyle\int_{\Delta\nu_F}P'_\nu\,d\nu}{\Delta\nu_F} \tag{27}$$

It should be noted that equation (27) between the apparent average absorption coefficient and the apparent spectral coefficient is of the same form as equations (25) and (25a) relating the true average coefficients to the spectral line strengths.

Empirical proof of the existence of an average apparent absorption coefficient can be obtained by comparison of the values of $\bar{k}'_F$ calculated by means of equations (27) and (29), respec tively. Data for equation (27) was obtained by numerical integration of figure (4), which resulted in a value for the $\displaystyle\int_{\Delta\nu_F}P'_\nu\,d\nu$ of 965.2 (meter-atm-cm)$^{-1}$. The effective

band width was chosen as 198 cm^{-1}. Substitution of these values in
equation (27) yielded a value of $\bar{k}_F^! = 5.03$ $(meter-atm)^{-1}$ for the
average apparent absorption coefficient. For evaluation of the aver-
age coefficient by means of equation (29), suitable band limits were
chosen by inspection of the transmission records for the various pres-
sures, and the areas under the transmission lines between these limits
were obtained by numerical integration. The ratios of the integrated
percentage of absorption were then plotted as functions of pressure
in figure (5) and the slope of the line noted. Substitution in equa-
tion (29) gave a value of 4.78 $(meter-atm)^{-1}$ for $\bar{k}_F^!$. The approximate
equality of the two values for $\bar{k}_F^!$ may be taken as proof of the exist-
ence of an average apparent absorption coefficient.

The average apparent absorption coefficient is related to the
true average absorption coefficient, which can be expressed in terms
of the sum of the individual line strengths according to equation (25),
in a complicated fashion depending upon instrumental resolution. How-
ever, since the rotational spacing and resolution for studies of the
apparent absorption coefficients of $CO^{(6)}$ and NO were similar, it is
reasonable to assume that the true average absorption coefficient bears
the same relation to the apparent average absorption coefficient for
these two gases. This ratio has been found to be 23 for CO^*. It is
therefore recommended, that an average absorption coefficient $\bar{k}_F$
23×5.03 $(meter \times atm)^{-1} = 115.69$ $(meter \times atm)^{-1}$ be used for radiant
heat transfer calculations on NO until more reliable experimental
measurements become available.

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*Unpublished results obtained by S. S. Penner and D. Weber

The temperature dependence of $\bar{k}_F$ can be calculated by use of equations (15) and (25). Reference to these two relations indicates that

$$\frac{\bar{k}_F(T_2)}{\bar{k}_F(T_1)} = \frac{\Delta V_F(T_1)}{\Delta V_F(T_2)} \cdot \frac{T_1}{T_2} \tag{33}$$

since the number of molecules per unit volume, N_T, varies inversely as the absolute temperature for an ideal gas.

IV. APPROXIMATE RADIANT HEAT TRANSFER CALCULATIONS FOR DIATOMIC GASES

This section contains an outline of the method[6] developed at the
Jet Propulsion Laboratory for making approximate radiant heat transfer
calculations for diatomic gases with specific application to nitric
oxide. The existence and the value of the average absorption coefficient
having been dealt with at length in Section III, it is assumed that this
coefficient exists and is known for the fundamental vibration-rotation
band as a function of temperature. Equation (23)

$$\varepsilon' = (1 - e^{-\bar{k}_F \, p.l.}) \frac{\int_{\lambda_{min}}^{\lambda_{max}} I_\lambda d\lambda}{\int_0^{+\infty} I_{o\lambda} \, d\lambda} + (1 - e^{-\bar{k}_{F.O.} \, pl}) \frac{\int_{\lambda'_{min}}^{\lambda'_{max}} I_\lambda d\lambda}{\int_0^{+\infty} I_{o\lambda} \, d\lambda} + \dots \quad (23)$$

will be used to calculate the effective emissivity.

Examination of equation (23) indicates that the calculation of
emissivities requires the determination of the band limits. Although
pressure has the effect of broadening the individual lines, the indi-
vidual line strength remaining constant, it is obvious that pressure
will have practically no effect on the effective band width. This con-
clusion follows since broadening a line whose strength is negligibly
small cannot have an appreciable effect on the band width. It is pos-
sible, however, in the case of extremely high pressures, to have a
line of significant strength broadened sufficiently to cause a measur-
able widening of the band. The present method of calculation is,

therefore, not suitable for pressures greater than a few hundred
atmospheres.

Before proceeding a description of the physical appearance of the
absorption band of NO and a statement of the relation between the com-
ponent parts of the band and particular transitions are of interest.
The band is composed of three distinct branches designated as the P, Q,
and R branches, respectively. The P-branch is the high frequency
branch, the R-branch is the low frequency branch, and the Q-branch forms
the center of the band and joins the P- and R-branches. The rotational
transitions $j-1 \rightarrow j$ are responsible for the R-branch, the transitions
$j \rightarrow j-1$ for the P-branch, and the transitions $j \rightarrow j$ for the Q-branch.
The number of rotational transitions associated with line strengths
large enough to contribute appreciably to radiation from the P- and
R-branches is the same, as can be shown by a detailed analysis of the
dependence of line strength on rotational quantum number.[6]

It is well known that a factor of the type $j \exp(-E_{o,j}/kT)$ or
$j \exp(-E_{o,j}/kT)$ is the dominant term depending on j in the expression
for line strength. Use can be made of this fact, if as a first approx-
imation, the band limits are chosen as those points at which the strengths
of the individual rotational lines tend to zero. The criterion used
for the proper choice of j_{max} was arbitrarily chosen as that value of
j for which $j \exp(-E_{o,j}/kT)$ corresponds approximately to 10^{-3} of the
maximum value of $j \exp(-E_{o,j}/kT)$. A study of figures (6) through (11)
in which $j \exp(-E_{o,j}/kT)$ has been plotted as a function of j at 300,
1000, 1500, 2000, 2500, 3000° K indicates that no very great difference

in j_{max} results if the value of j_{max} is set equal to the value of j for which $j \exp(-E_{o,j}/kT)$ has decreased to 10^{-2} or 10^{-4} of its maximum value. It should be noted that the emissivity does not depend critically on the value of j_{max} because the uncertainty in the value of j_{max} is partly compensated for by a larger or smaller average absorption coefficient if too small or too large a value has been chosen, respectively, for j_{max}. Band emissivity calculations have been carried out for values of j_{max} corresponding to somewhat different criteria for choosing j_{max}. By the use of figures (6) through (11) the values of j_{max_1} and j_{max_2} given in Table II were obtained for calculating the probable effective band widths where j_{max_1} corresponds to the value of j for which $j \exp(-E_{o,j}/kT)$ has decreased to approximately 10^{-3} of its maximum value.

TABLE II

THE VALUES OF j_{max_1} and j_{max_2} AS A FUNCTION OF TEMPERATURE

T	j_{max_1}	j_{max_2}
300	30	33
1000	54	58
1500	65	69
2000	77	81
2500	88	91
3000	100	106

By use of the familiar quantum relation the approximate band limits of
the fundamental can, therefore, be determined as follows:

$$\underset{\substack{n \to n-1 \\ j \to j-1}}{V_{max}} = \frac{E(n, j_{max}) - E(n-1, j_{max} - 1)}{h c} \tag{34}$$

$$\underset{\substack{n \to n-1 \\ j-1 \to j}}{V_{min}} = \frac{E(n, j_{max} - 1) - E(n-1, j_{max})}{h c} \tag{34a}$$

The energy levels of NO can be calculated from following relation

$$\frac{E(n,j)}{hc} = (n+\tfrac{1}{2})\omega_e - (n+\tfrac{1}{2}) x_e \omega_e + j(j+1) B_e - j^2(j+1)^2 D_e - (n+\tfrac{1}{2})j(j+1) \propto \tag{35}$$

where ω_e, B_e, D_e, x_e and $\propto$ are well-known constants for NO determined from
spectroscopic measurements. The following numerical values were used
for NO: ω_e = 1906.5 cm^{-1}; x_e = 0.7564 x 10^{-2}; B_e = 1.7006 cm^{-1}
D_e = 5.4124 cm^{-1}; $\propto$ = 1.8366 x 10^{-2}cm^{-1} [23]. The spectroscopic data
for NO has recently been revised by Gillette and Eyster[21]. However,
for the present purposes, the data given by Sponer are sufficiently
accurate. The approximate band limits of the fundamental of NO as
calculated from equations (34) and (34a) are tabulated below as func-
tions of temperature for the values of j_{max_1};

TABLE III

APPROXIMATE BAND LIMITS FOR THE FUNDAMENTAL OF NO

T	j_{max_1}	ν_{max}, cm^{-1}	ν_{min}, cm^{-1}	$\Delta\nu$ cm^{-1}	λ_{max}, cm	λ_{min}, cm
300	30	1961.5	1760.9	200.6	5.6789	5.0981
1000	54	2002.7	1645.8	356.9	6.0761	4.9932
1500	65	2012.8	1587.4	425.4	6.2996	4.9682
2000	77	2018.3	1519.4	498.9	6.5815	4.9547
2500	88	2016.8	1454.0	562.8	6.8776	4.9583
3000	100	2009.3	1379.4	629.9	7.2495	4.9768

A study of Table II indicates that as T, and therefore j_{max} increases, λ_{min} passes through a minimum (bandhead) somewhere between 1500 and 2500°K and thereafter increases with temperature. It can be seen that since λ_{min} is a double-valued function of j the effect of choosing a j_{max} value larger than that corresponding to the bandhead has the effect of eliminating a number of transitions which contribute materially to radiant heat transfer. Therefore, in order to avoid this difficulty the value of j corresponding to the bandhead should be used for those temperatures where the calculated value of j_{max} is larger than the j value corresponding to the bandhead.[6] The value of j_{max} corresponding to the bandhead was accurately determined as $j_{max} = 80$ by noting the maximum of the $j \rightarrow j - 1$ transitions. Tables IV and V contain the band limits for the fundamental band of NO for j_{max_1} and j_{max_2}, with proper allowance for the existence of the bandhead.

TABLE IV

BAND LIMITS OF FUNDAMENTAL OF NITRIC OXIDE

CALCULATED FROM THE VALUE OF j_{max_1}

T	j_{max_1}	$V_{max},$ cm^{-1}	$V_{min},$ cm^{-1}	$\Delta V,$ cm^{-1}	$\lambda_{max},$ cm	$\lambda_{min},$ cm
300	30	1961.5	1760.9	200.6	5.6789	5.0981
1000	54	2002.7	1645.8	356.9	6.0761	4.9932
1500	65	2012.8	1587.4	425.4	6.2996	4.9682
2000	77	2018.3	1519.4	498.9	6.5815	4.9547
2500	80-88	2018.8	1454.0	564.8	6.8776	4.9534
3000	80-100	2018.8	1379.4	639.4	7.2495	4.9534

TABLE V

BAND LIMITS OF FUNDAMENTAL OF NITRIC OXIDE

CALCULATED FROM THE VALUES OF j_{max_2}

T	j_{max_2}	$V_{max},$ cm^{-1}	$V_{min},$ cm^{-1}	$\Delta V,$ cm^{-1}	$\lambda_{max},$ cm	$\lambda_{min},$ cm
300	33	1968.0	1747.5	220.5	5.7225	5.0813
1000	58	2007.2	1625.1	382.1	6.1535	4.9821
1500	69	2015.3	1565.7	449.6	6.3869	4.9620
2000	80-81	2018.8	1496.2	522.6	6.6866	4.9534
2500	80-91	2018.8	1435.8	583.0	6.9648	4.9534
3000	80-106	2018.8	1340.7	678.1	7.4588	4.9534

Detailed examination of the line strength[6] indicates that the overtone will decrease to 10^{-3} of its maximum value at approximately the same value of j_{max} as the fundamental. The same j_{max} values have, therefore, been used for the first overtone as for the fundamental. Tables V and VI summarize the band limits for the first overtone of NO corrected for the bandhead for the two choices of j_{max}. The bandhead in the case of the first overtone, determined by the same detailed calculations as for the fundamental, occurred at $j_{max} = 44$.

TABLE VI

BAND LIMITS OF FIRST OVERTONE OF NITRIC OXIDE

CALCULATED FROM THE VALUES OF j_{max_1}

T	j_{max_1}	V'_{max}, cm^{-1}	V'_{min}, cm^{-1}	$\Delta V'_{cm}^{-1}$	λ'_{max}, cm	λ'_{min}, cm
300	30	3793.4	3593.9	199.5	2.7825	2.6362
1000	44-54	3800.7	3442.1	358.6	2.9052	2.6311
1500	44-65	3800.7	3360.0	440.7	2.9762	2.6311
2000	44-77	3800.7	3260.3	540.4	3.0672	2.6311
2500	44-88	3800.7	3162.2	638.5	3.1624	2.6311
3000	44-100	3800.7	3045.9	754.8	3.2831	2.6311

TABLE VII

BAND LIMITS OF FIRST OVERTONE OF NITRIC OXIDE

CALCULATED FROM THE VALUES OF j_{max_2}

T	j_{max_2}	V_{max}, cm^{-1}	V_{min}, cm^{-1}	ΔV, cm^{-1}	λ_{max}, cm	λ_{min}, cm
300	33	3796.0	3577.0	219.0	2.7956	2.6344
1000	44-58	3800.7	3412.0	388.7	2.9300	2.6311
1500	44-69	3800.7	3328.3	472.4	3.0045	2.6311
2000	44-81	3800.7	3226.1	574.6	3.0997	2.6311
2500	44-91	3800.7	3134.0	666.7	3.1908	2.6311
3000	44-106	3800.7	2985.0	815.7	3.3350	2.6311

In figures (12) and (13) the effective band limits are shown as a function of temperature for the NO fundamental and first overtone of NO, respectively.

The band limits having been found, the intensity ratios, $\int_{\Delta\lambda} J_\lambda \, d\lambda / \int_0^{+\infty} J_\lambda \, d\lambda$, in equation (23) can readily be evaluated by the use of Planck's radiation functions. An abbreviated table of these functions is shown in Table VIII. The intensity ratios have been plotted for the fundamental and first overtone of NO as functions of temperature in figure (14). It should be noted that these ratios represent the maximum attainable values of the contributions to the total emissivity for a given vibration-rotation band, and that, therefore, their sum represents the total maximum emissivity. Figure (14) indicates that the peak emissivity for

the fundamental occurs at approximately 850° K and for the first over-
tone at 1500° K. These results can be understood qualitatively in
terms of the temperature dependence of the wave length at which the in-
tensity of radiation is a maximum (Wien's displacement law).

The average absorption coefficient for the fundamental can be cal-
culated at different temperatures by means of equation (33). Similar
calculations can be made to determine the average absorption coeffic-
ient for the first overtone as a function of temperature if the room
temperature value of $\overline{k}_{F.O.}$ is known. If the room temperature value of
$\overline{k}_F$ has not been determined experimentally, then it can be calculated,
approximately, by an equation given by Rosenthal[24],

$$\frac{\overline{k}_{F.O.}}{\overline{k}_F} = \frac{x_e(1-5x_e)}{(1-3x_e)^2} \tag{36}$$

where x_e is the anharmonicity constant which has a value of 0.756×10^{-2}
for NO. Using equation (36) and the value for the fundamental average
absorption coefficient of 115.69 (meter-atm)$^{-1}$, the value of first over-
tone average coefficient at room temperature is found to be 83.09×10^{-2}
(meter-atm)$^{-1}$.

The necessary information is now available to calculate the emiss-
ivity of NO as a function of temperature. Because of the uncertainties
in the numerical value of $\overline{k}_F$ discussed in section III, emissivity tables
have not been calculated for NO. However, in order to facilitate the
use of the results described in this thesis for making approximate emiss-
ivity calculations, the procedure for determining the emissivity of NO

as a function of temperature is outlined again in some detail.

The Calculation of the Emissivity of NO

The emissivity of NO is given by the approximate relation

$$\dot{\mathcal{E}}' = (1 - e^{-\bar{k}_F p l}) \frac{\displaystyle\int_{\lambda min}^{\lambda max} I_\lambda \, d\lambda}{\displaystyle\int_0^{+\infty} I_{0\lambda} \, d\lambda} + (1 - e^{-\bar{k}_{F.O.} p l}) \frac{\displaystyle\int_{\lambda'min}^{\lambda'max} I_\lambda \, d\lambda}{\displaystyle\int_0^{+\infty} I_{0\lambda} \, d\lambda} + \ldots \quad (23)$$

The ratios $\displaystyle\int_{\lambda min}^{\lambda max} I_\lambda \, d\lambda \Big/ \int_0^{+\infty} I_{0\lambda} \, d\lambda$ and $\displaystyle\int_{\lambda'min}^{\lambda'max} I_\lambda \, d\lambda \Big/ \int_0^{+\infty} I_{0\lambda} \, d\lambda$

are plotted in figure (14) as functions of temperature. The value of $\bar{k}_F$ can be calculated as a function of temperature from the relation

$$\bar{k}_F(T_2) = \frac{\Delta \nu_F(T_1)}{\Delta \nu_F(T_2)} \cdot \frac{T_1}{T_2} \, \bar{k}_F(T_1)$$

similarly,

$$\bar{k}_{F.O.}(T_2) = \frac{\Delta \nu_{F.O.}(T_1)}{\Delta \nu_{F.O.}(T_2)} \cdot \frac{T_1}{T_2} \cdot \bar{k}_{F.O.}(T_1)$$

The effective band widths $\Delta \nu_F$ and $\Delta \nu_{F.O.}$ are given, as a function of temperature, in tables VI and VII. The recommended values for the average absorption coefficients at 300° K are

$$\bar{k}_F = 115.69 \, (m \times atm)^{-1}$$

$$\bar{k}_{F.O.} = 83.09 \times 10^{-2} \, (m \times atm)^{-1}$$

The values of $\bar{k}_F$ and $\bar{k}_{F.O.}$ are not known accurately at the present time and may require revision as the result of current experimental studies.

If the values of the average absorption coefficients are changed, the method of calculating ε' remains unaltered except for the use of the new values of $\bar{k}_P$ and $\bar{k}_{P.0}$.

TABLE VIII

PLANCK'S RADIATION FUNCTIONS

$$\frac{R_0 - \lambda}{R_0 - \infty} = F \times 10^{-p} \qquad\qquad \frac{R_0 - \lambda}{R_0 - \infty} = F \times 10^{-p}$$

λT IN CM K°	F	p	λT IN CM K°	F	p
0.050	1.3652	9	0.090	8.9269	5
.051	2.2642	9	.091	1.0314	4
.052	3.6788	9	.092	1.1874	4
.053	5.8629	9	.093	1.3626	4
.054	9.1749	9	.094	1.5586	4
.055	1.4113	8	.095	1.7772	4
.056	2.1358	8	.096	2.0204	4
.057	3.1829	8	.097	2.2901	4
.058	4.6745	8	.098	2.5885	4
.059	6.7710	8	.099	2.9179	4
			.100	3.2804	4
.060	9.6798	8			
.061	1.3667	7	0.100	3.2804	4
.062	1.9069	7	.105	5.6770	4
.063	2.6307	7	.110	9.2957	4
.064	3.5907	7	.115	1.4510	3
			.120	2.1727	3
.065	4.8510	7			
.066	6.4902	7	.125	3.1370	3
.067	8.6028	7	.130	4.3866	3
.068	1.1302	6	.135	5.9631	3
.069	1.4723	6	.140	7.9053	3
			.145	1.0248	2
.070	1.9025	6			
.071	2.4393	6	.150	1.3023	2
.072	3.1045	6	.155	1.6254	2
.073	3.9230	6	.160	1.9962	2
.074	4.9236	6	.165	2.4161	2
			.170	2.8858	2
.075	6.1392	6			
.076	7.6070	6	.175	3.4056	2
.077	9.3692	6	.180	3.9754	2
.078	1.1473	5	.185	4.5944	2
.079	1.3971	5	.190	5.2613	2
			.195	5.9749	2
.080	1.6923	5			
.081	2.0393	5	.200	6.7331	2
.082	2.4453	5	.205	7.5339	2
.083	2.9183	5	.210	8.3750	2
.084	3.4668	5	.215	9.2538	2
			.220	1.0168	1
.085	4.1002	5			
.086	4.8287	5	.225	1.1114	1
.087	5.6633	5	.230	1.2091	1

TABLE VIII

PLANCK'S RADIATION FUNCTIONS (Cont'd)

$$\frac{R_0 - \lambda}{R_0 - \infty} = F \times 10^{-P} \qquad\qquad \frac{R_0 - \lambda}{R_0 - \infty} = F \times 10^{-P}$$

λT IN CM K^o	F	P	λT IN CM K^o	F	P
.088	6.6159	5	.235	1.3094	1
.089	7.6993	5	.240	1.4122	1
			.245	1.5171	1
0.250	1.6239	1	0.500	6.3494	1
.255	1.7324	1	.510	6.4727	1
.260	1.8423	1	.520	6.5912	1
.265	1.9533	1	.530	6.7051	1
.270	2.0653	1	.540	6.8146	
.275	2.1780	1	.550	6.9198	1
.280	2.2911	1	.560	7.0209	1
.285	2.4047	1	.570	7.1182	1
.290	2.5183	1	.580	7.2116	1
.295	2.6320	1	.590	7.3014	1
			.600	7.3877	1
.300	2.7454	1			
.305	2.8585	1	.600	7.3877	1
.310	2.9712	1	.620	7.5505	1
.315	3.0833	1	.640	7.7010	1
.320	3.1947	1	.660	7.8402	1
			.680	7.9691	1
.325	3.3053	1			
.330	3.4150	1	.700	8.0885	1
.335	3.5237	1	.720	8.1993	1
.340	3.6314	1	.740	8.3020	1
.345	3.7379	1	.760	8.3974	1
			.780	8.4861	1
.350	3.8432	1			
.355	3.9474	1	.800	8.5687	1
.360	4.0502	1	.820	8.6455	1
.365	4.1517	1	.840	8.7172	1
.370	4.2518	1	.860	8.7840	1
			.880	8.8465	1
.375	4.3506	1			
.380	4.4479	1	.900	8.9043	1
.385	4.5438	1	.920	8.9494	1
.390	4.6382	1	.940	9.0105	1
.395	4.7312	1	.960	9.0584	1
.400	4.8227	1	.980	9.1033	1
			1.000	9.1455	1
.400	4.8327	1			
.410	5.0012	1	1.00	9.1455	1
.420	5.1738	1	1.05	9.2402	1
.430	5.3404	1	1.10	9.3217	1
.440	5.5012	1	1.15	9.3921	1
			1.20	9.4532	1

TABLE VIII

PLANCK'S RADIATION FUNCTIONS (Cont'd)

$$\frac{R_{O-\lambda}}{R_{O-\infty}} = F \times 10^{-P} \qquad\qquad \frac{R_{O-\lambda}}{R_{O-\infty}} = F \times 10^{-P}$$

λT IN CM K°	F	p	λT IN CM K°	F	p
.450	5.6563	1			
.460	5.8057	1	1.25	9.5065	1
.470	5.9495	1	1.30	9.5531	1
.480	6.0880		1.35	9.5942	1
.490	6.2212	1	1.40	9.6304	1
			1.45	9.6624	1
			1.50	9.6909	1
			1.55	9.7163	1
			1.60	9.7390	1
			1.65	9.7594	1
			1.70	9.7777	1
			1.75	9.7942	1
			1.80	9.8091	1
			1.85	9.8226	1
			1.90	9.8349	1
			1.95	9.8461	1
			2.00	9.8563	1

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TABLE OF SYMBOLS

A_ν — intensity of light absorbed

$A_{i \to j}$ — Einstein coefficient of spontaneous emission

A_M — area under rotational line

$B_{i \to j}$ — Einstein coefficient of induced emission

$B_{j \to i}$ — Einstein coefficient of induced absorption

c — velocity of light

E — energy

h — Planck's constant

i — upper energy level

I_ν — intensity of transmitted light

$I_{o\nu}$ — intensity of incident light

j — lower energy level; rotational quantum number

k — Boltzmann's constant

$\bar{k}_F$ — True average absorption coefficient for fundamental

$\bar{k}_{F.O.}$ — True average absorption coefficient for first overtone

$\bar{k}'_F$ — Apparent average absorption coefficient for fundamental

$\bar{k}'_{F.O.}$ — Apparent average absorption coefficient for first overtone

l — path length

N — molecular population

n — vibrational quantum number

p — pressure

pl — optical density

P_ν — True spectral absorption coefficient

P_ν' — Apparent absorption coefficient

T — Absolute temperature

GREEK SYMBOLS

δ -   Spectral half-width

ε -   effective charge

ε' -   effective emissivity

ε_ν -   spectral emissivity

λ -   wave length

μ -   reduced mass; microns

ν -   wave number, frequency

ν_o -   frequency corresponding to $n = 0 \rightarrow n = 1$; $j = 0 \rightarrow j = 0$

$\rho(\nu)$ -   density of radiation of blackbody

$\rho'(\nu)$ -   external density of radiation

$\int P_\nu d\kappa$ line strength in absorption

UNITS

$A_{i \to j}$ — $(cc \times sec)^{-1}$

$B_{i \to j};\ B_{j \to i}$ — $(erg \times sec \times sec)^{-1}$

P_ν — $(meter \times atm)^{-1}$

$\int P_\nu\, d\nu$ — $(meter \times atm \times cm)^{-1}$

$\int I_\nu\, d\nu$ — $ergs/cc \times sec$

$\rho(\nu)$ — $erg \times sec/cc$

ν — cm^{-1}

λ — cm, microns

LIST OF FIGURES

WAVE LENGTH CALIBRATION
CURVE FOR PERKIN-ELMER
MODEL 12-C SPECTROMETER
WITH LITHIUM FLUORIDE
PRISM

FIGURE-1-

- 43 -

LOGARITHM OF PERCENTAGE

OF TRANSMISSION AS A

FUNCTION OF PRESSURE

FOR NO AT 1850.8 CM^{-1}

FIGURE—2—

PRESSURE, CM OF HG

$\log \left[100 \ I_v / I_{ov} \right]$

LOGARITHM OF PERCENTAGE OF TRANSMISSION AS A FUNCTION OF PRESSURE FOR NO AT 1936.1 CM^{-1}

FIGURE—3—

APPARENT ABSORPTION

COEFFICIENT OF NO AS A

FUNCTION OF WAVE NUMBER

(RESOLUTION 4 CM^{-1})

FIGURE-4-

WAVE NUMBER, ν , CM^{-1}

APPARENT ABSORPTION COEFFICIENT, P_i, (M×ATM)$^{-1}$

INTEGRATED PERCENTAGE OF
ABSORPTION AS A FUNCTION
OF PRESSURE FOR NO

FIGURE -5-

THE DEPENDENCE OF $j \exp(-E_{o,j}/kT)$

ON j FOR NO AT 300° K

FIGURE-6-

THE DEPENDENCE OF $j \exp(-\varepsilon_{o,j} / T)$
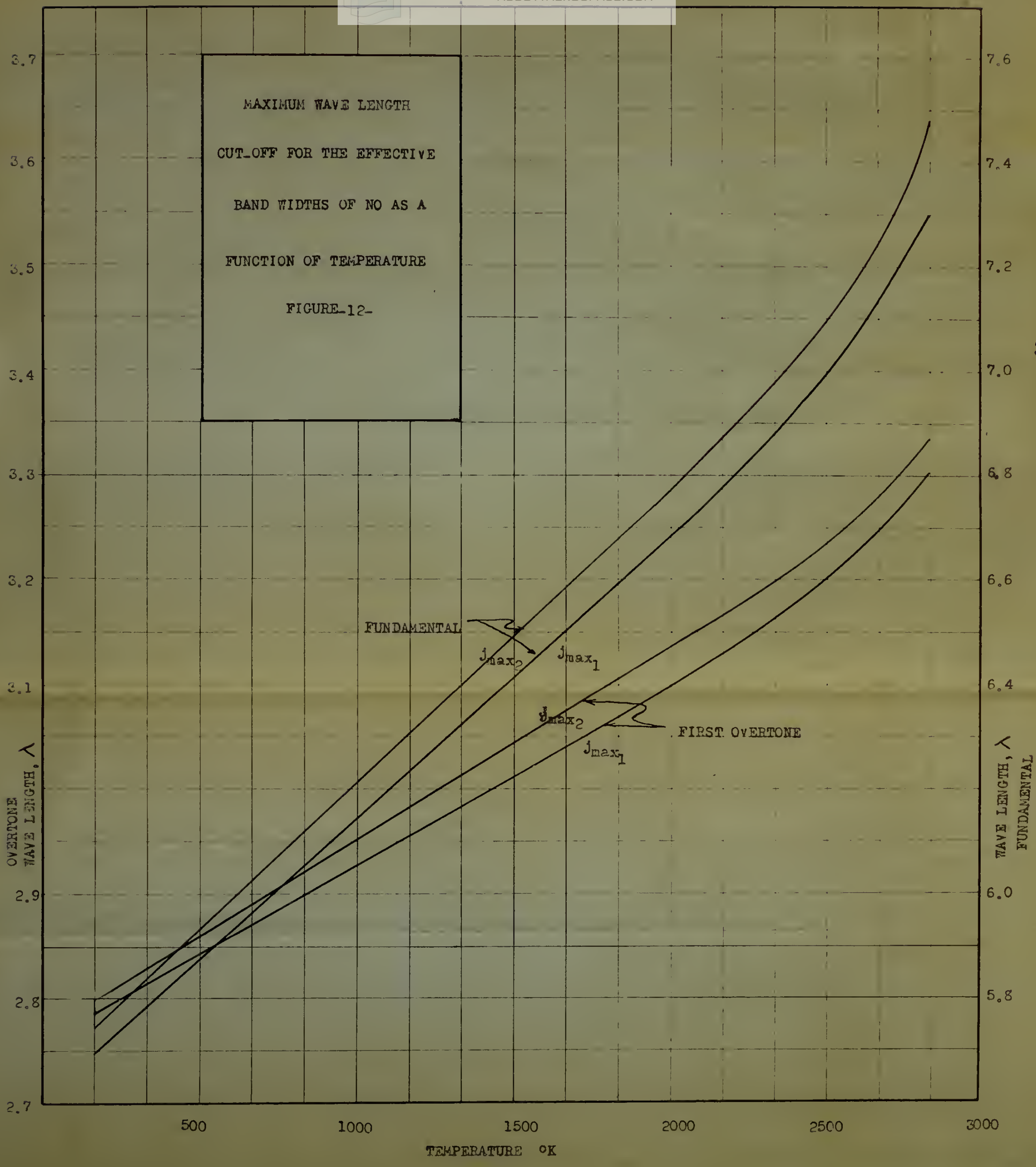
ON j FOR NO AT 1000° K

FIGURE-7-

QUANTUM NUMBER, j

THE DEPENDENCE OF $j \exp(-E_{0,j}/kT)$

ON j FOR NO AT 1500° K
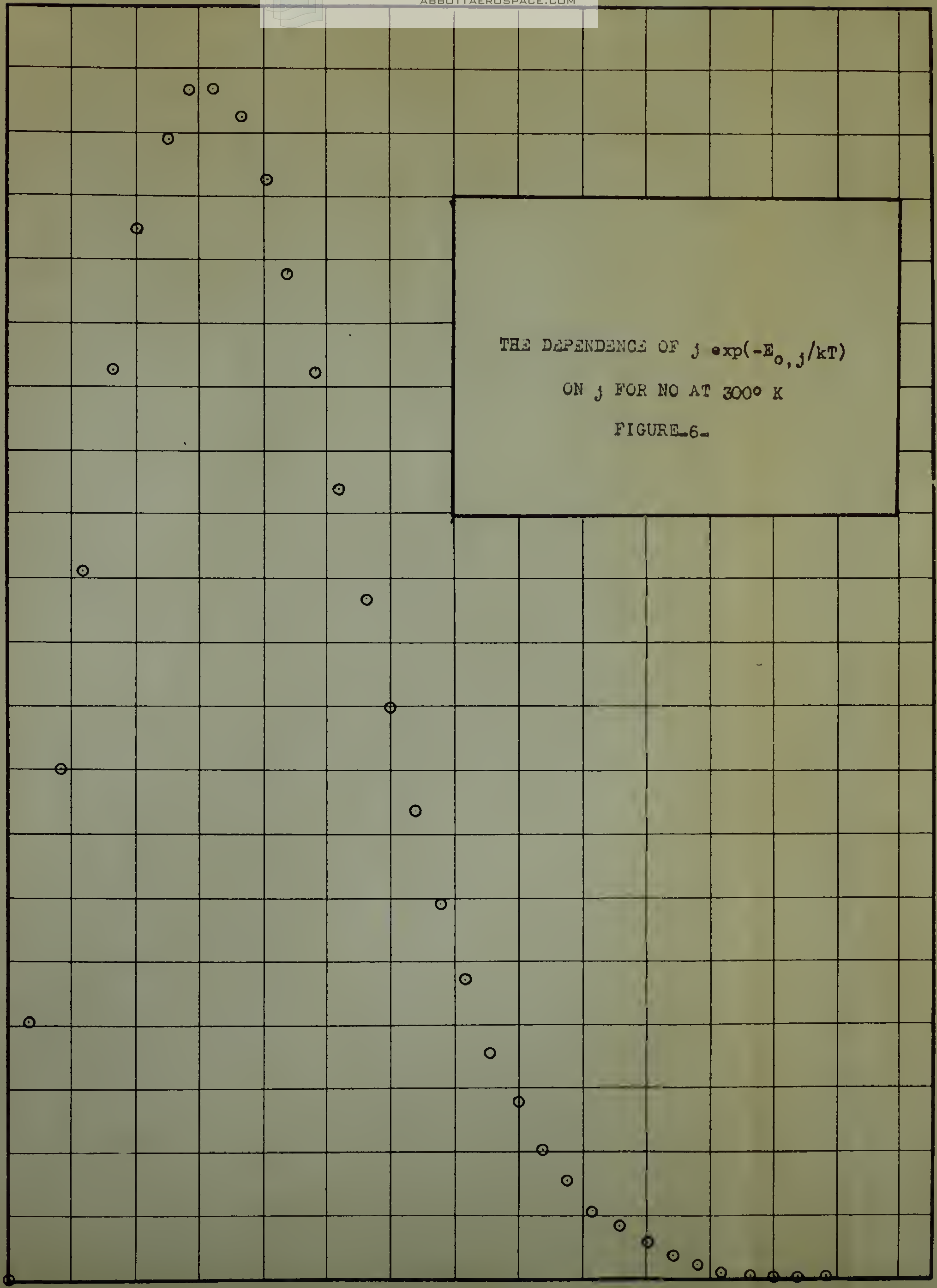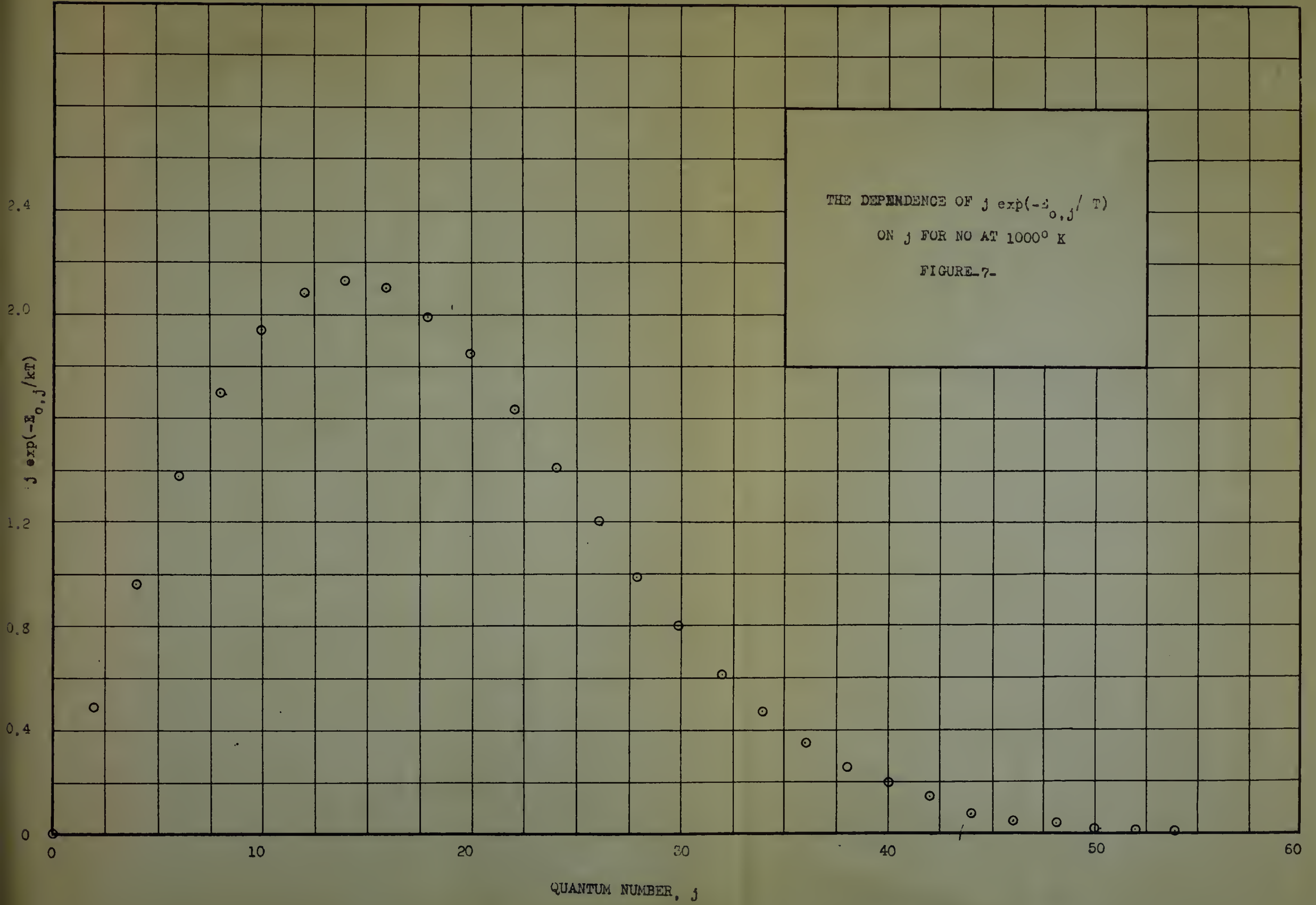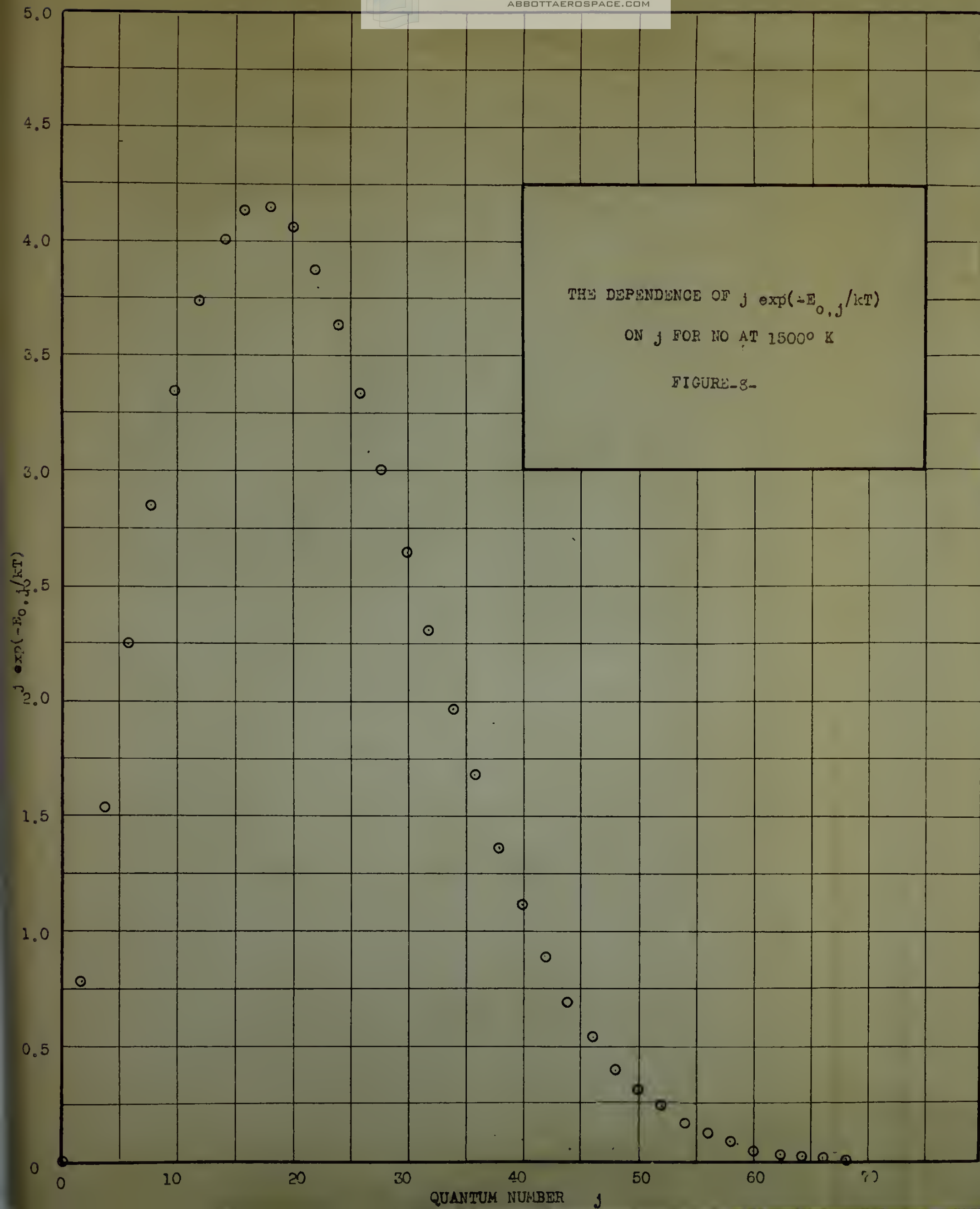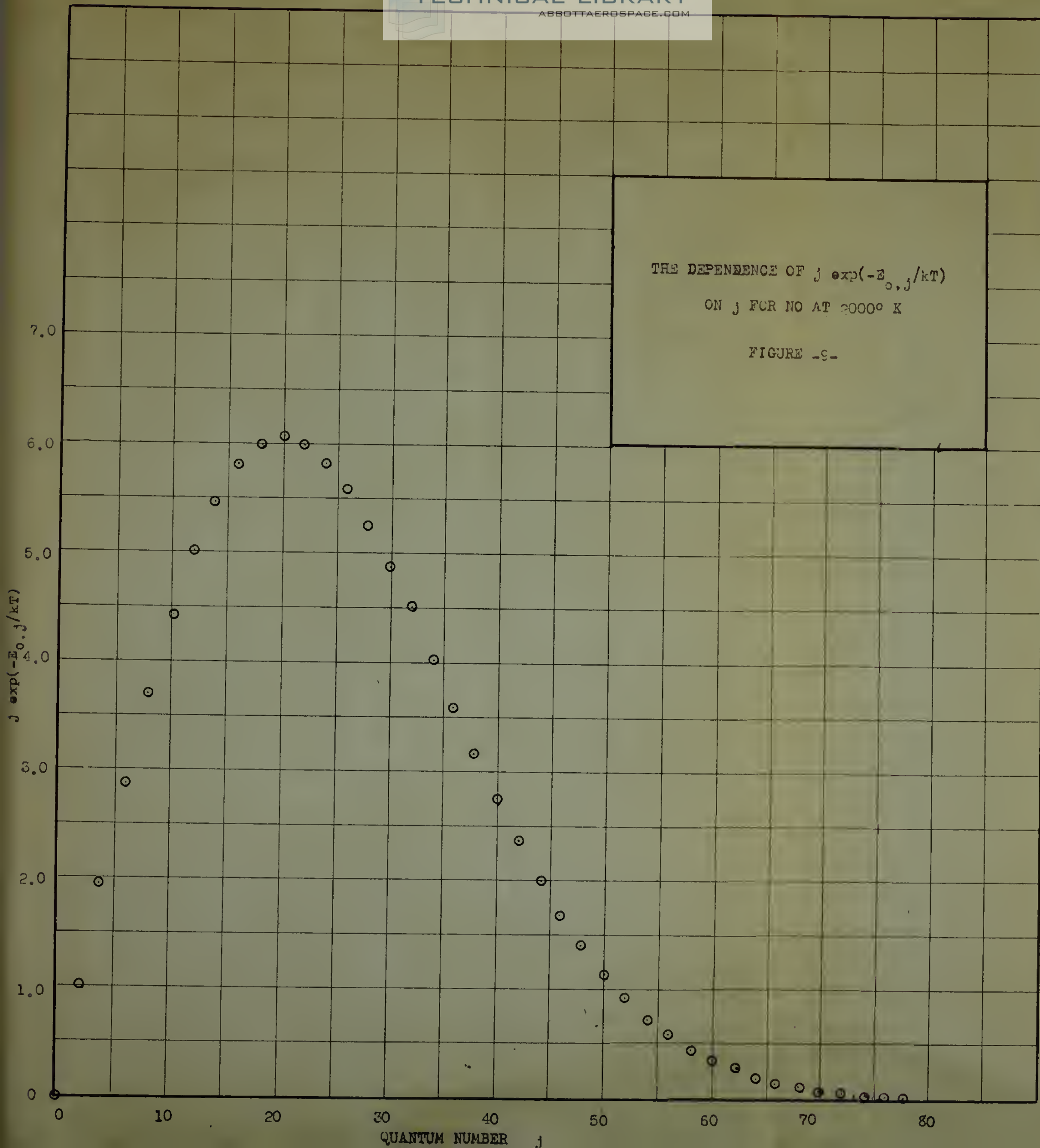
FIGURE-8-

THE DEPENDENCE OF $j \exp(-E_{o,j}/kT)$

ON j FOR NO AT $2000°$ K
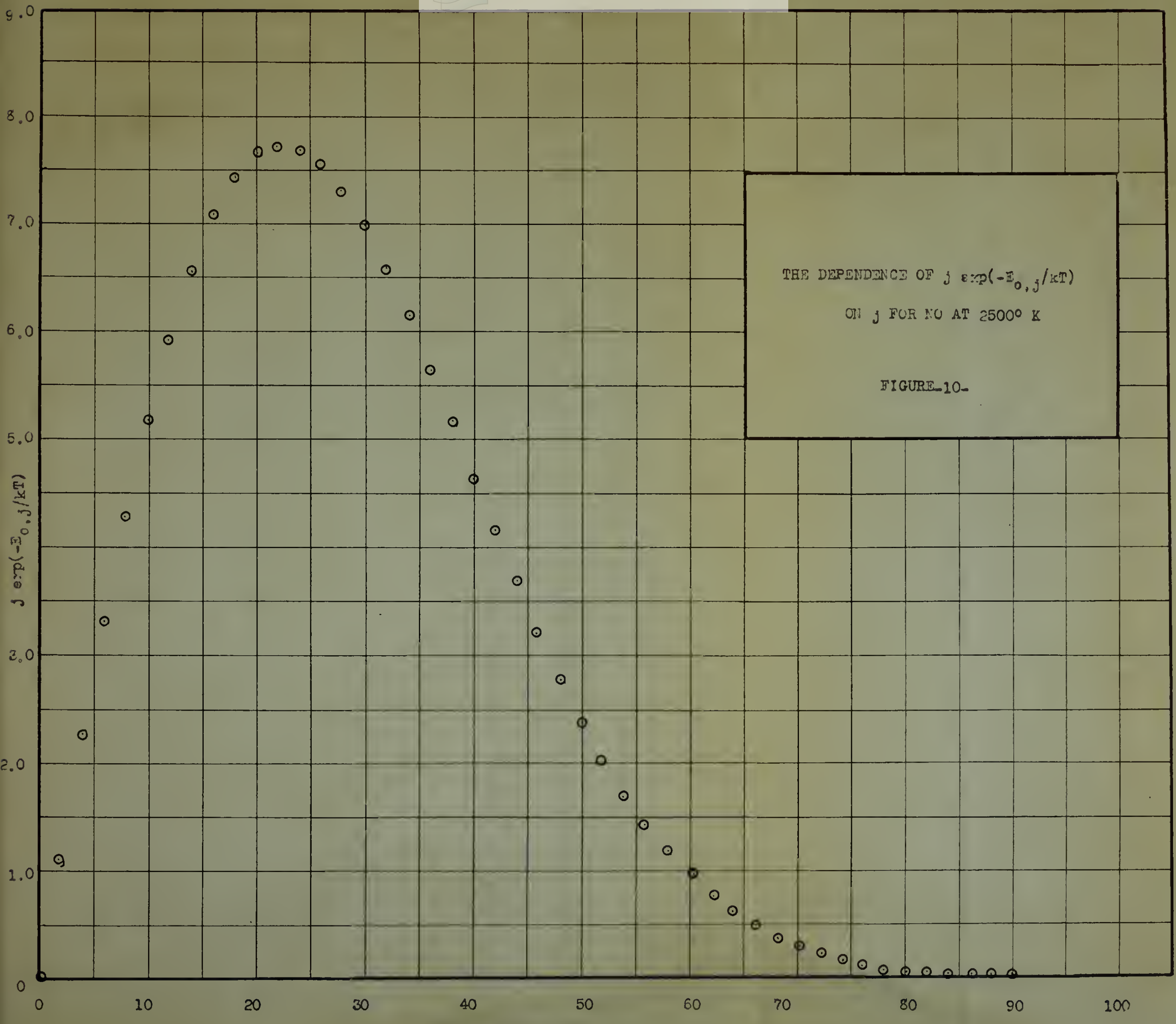
FIGURE _9_

THE DEPENDENCE OF $j \exp(-E_{0,j}/kT)$

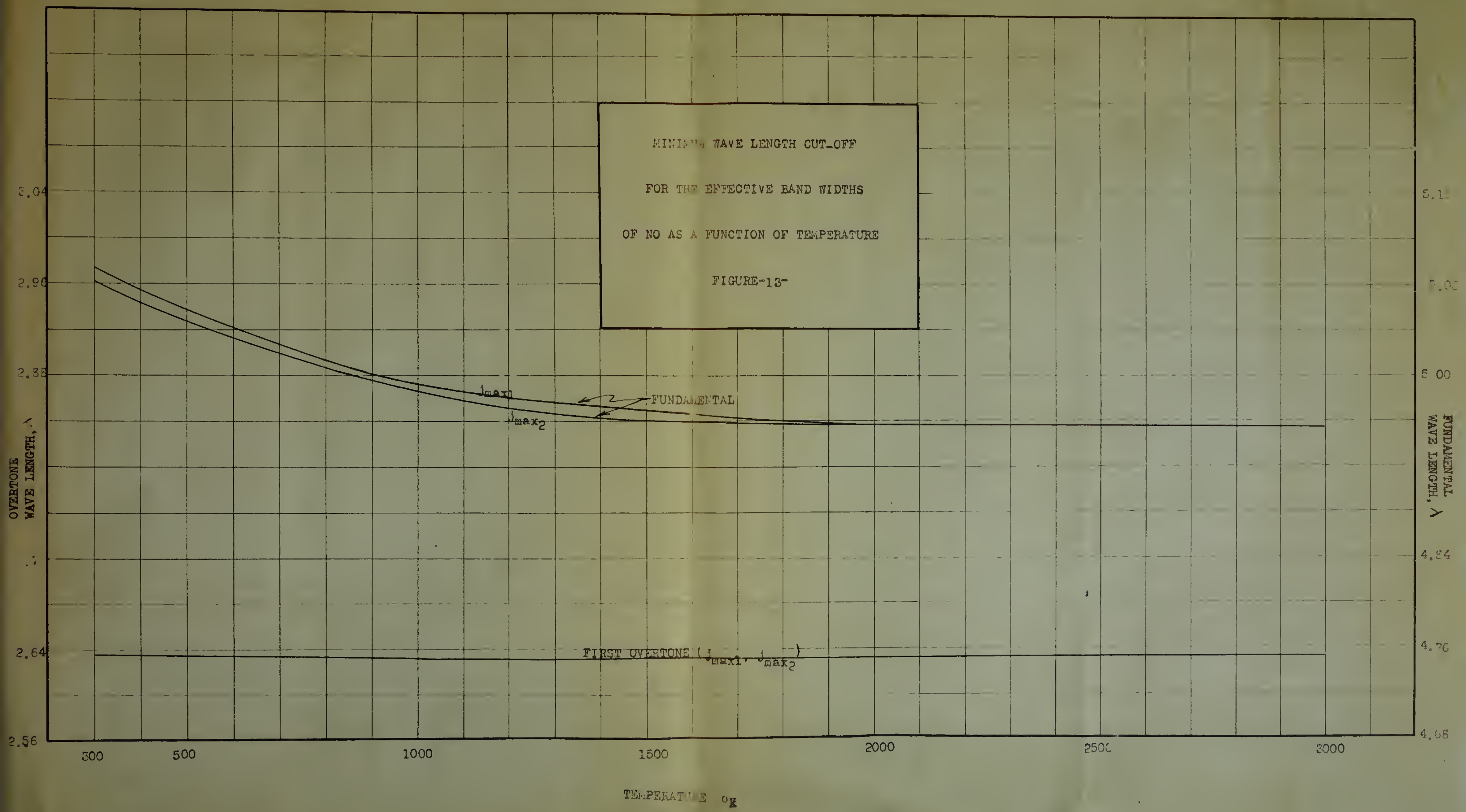ON j FOR NO AT $2500°$ K

FIGURE-10-

QUANTUM NUMBER j

THE DEPENDENCE OF $j \exp(-E_{o,j}/kT)$
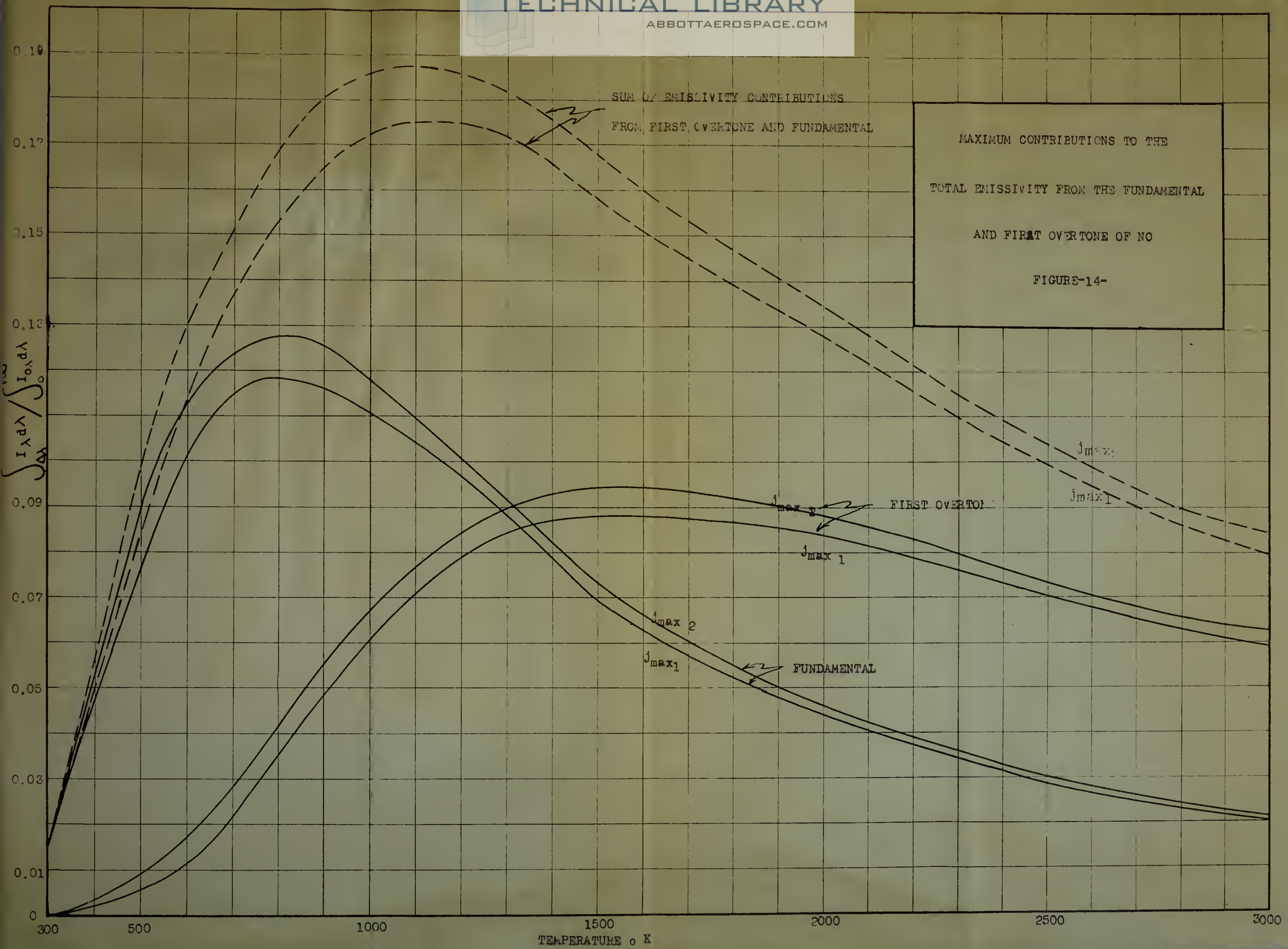
ON j FOR NO AT 3000° K

FIGURE-11-

MAXIMUM WAVE LENGTH

CUT-OFF FOR THE EFFECTIVE

BAND WIDTHS OF NO AS A

FUNCTION OF TEMPERATURE

FIGURE-12-

MINIMUM WAVE LENGTH CUT-OFF

FOR THE EFFECTIVE BAND WIDTHS

OF NO AS A FUNCTION OF TEMPERATURE

FIGURE-13-
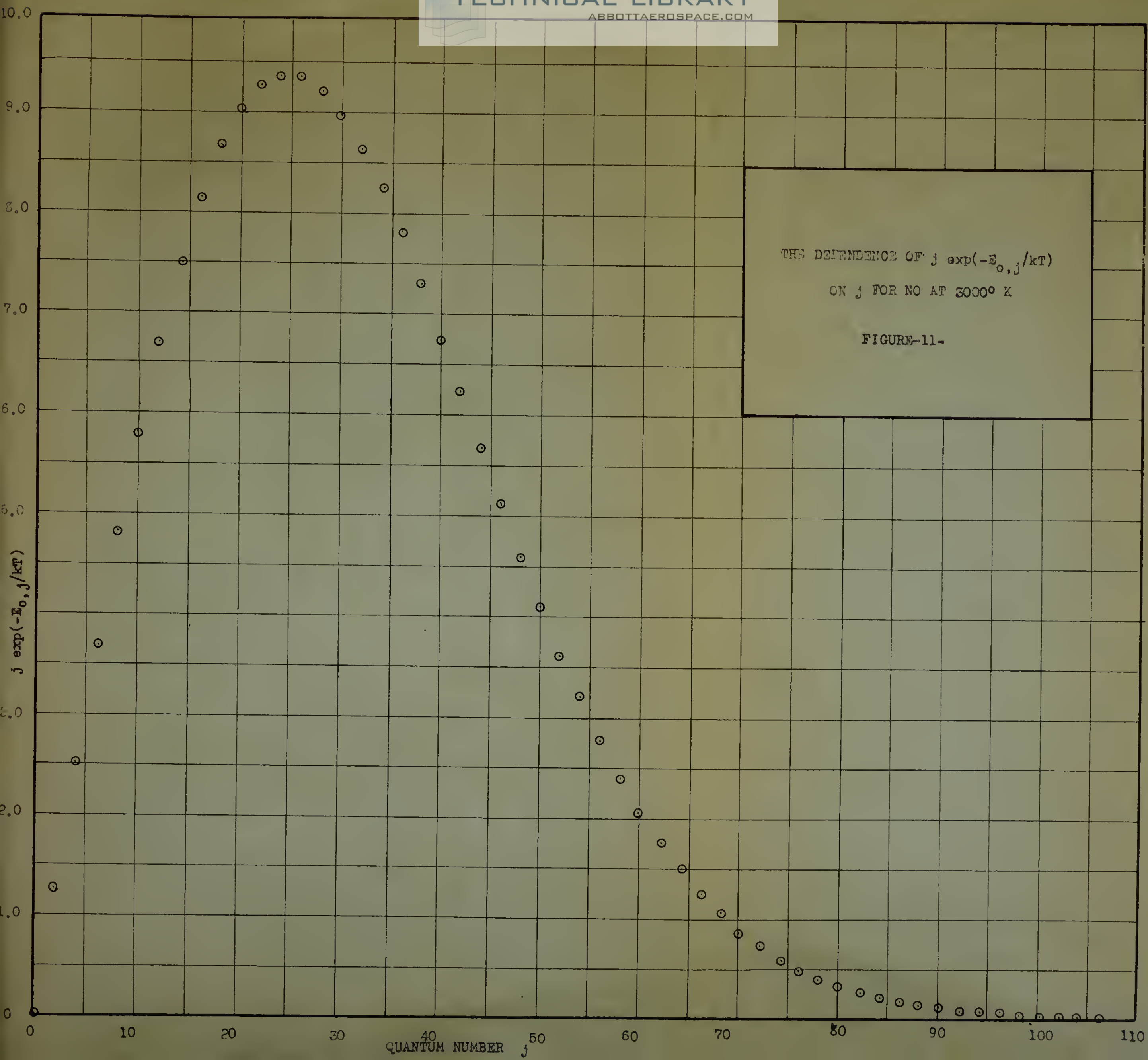
SUM OF EMISSIVITY CONTRIBUTIONS
FROM FIRST, OVERTONE AND FUNDAMENTAL

MAXIMUM CONTRIBUTIONS TO THE

TOTAL EMISSIVITY FROM THE FUNDAMENTAL

AND FIRST OVERTONE OF NO

FIGURE-14-