

ELECTRONIC TRANSITION MOMENTS FOR AIR MOLECULES

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Abstract—Electronic transition moments for molecular bands which radiate strongly in air, in the temperature range from 4000 to 9000°K, have been determined from available experimental data in conjunction with recently computed Franck–Condon factors. An analysis has also been made of the radiation in the infrared leading to effective Z^2 values for the free-free Kramers' radiation produced by electrons scattered from neutrals.

I. INTRODUCTION

OVER the past five years, the radiation from air, N_2 and O_2 has been the subject of numerous theoretical and experimental studies, an important aim of which has been to determine the electronic transition moments for the molecular bands which radiate strongly in the temperature range from 4000 to 9000°K. A variety of experimental techniques, including emission and absorption studies on shock heated air, room temperature absorption studies in pressurized cells, and lifetime measurements have been employed. The results of these experiments have often been reported in terms of f -numbers for the radiating bands. Since the definition of the f -number for a molecular band system is somewhat ambiguous and since different workers have not always followed the same convention, there has been a certain amount of confusion. In addition, the theoretical reduction of the data involves the use of calculated Franck–Condon factors and, as time has progressed, new and improved values of these factors have become available and used in the analysis. This too, had led to confusion. It was therefore felt that a comprehensive review and uniform analysis of the data might help to clarify the situation. In this paper, we have attempted to conduct such a review.

In section II, we have summarized the theoretical equations used in the analysis and reviewed the available calculations of Franck–Condon factors. In section III, we have reviewed the experimental data relating to the important molecular bands and computed electronic transition moments. Section IV presents some recent results on the Kramers' radiation from electrons scattered by neutrals. Section V discusses emissivity tables for air, and the final section contains a brief summary of the results.

II. GENERAL THEORY

In the present analysis, we shall consider only the equilibrium radiation from gases which are optically thin at all wavelengths. Under this condition, the spectral intensity of the radiation per unit volume is

$$\frac{dI}{dV d\Omega d\tilde{\nu}} = \mu'_\nu \frac{dB}{dA d\Omega d\tilde{\nu}} \quad (1)$$

where

$$\frac{dB}{dA d\Omega d\tilde{\nu}} = 2hc^2 \tilde{\nu}^3 \left[\exp \left(\frac{hc\tilde{\nu}}{kT} \right) - 1 \right]^{-1} \quad (2)$$

is the black body intensity,

$$\mu'_{\nu} = \mu_{\nu} \left[1 - \exp \left(-\frac{hc\tilde{\nu}}{kT} \right) \right] \quad (3)$$

is the apparent absorption coefficient, μ_{ν} is the true absorption coefficient and $\tilde{\nu}$ is the frequency in wave numbers.

For an isolated spectral line, the true absorption coefficient is related to the electronic f -number, f_{ij} , for the transition by the equation⁽¹⁾

$$\int_{\text{line}} \mu_{\nu} d\tilde{\nu} = \pi r_0 f_{ij} N_j \quad (4)$$

where $r_0 = e^2/mc^2$ is the classical electron radius and N_j is the number of particles in the absorbing state.

For transition between specified vibrational levels, $v'v''$, belonging to different electronic states of a molecule, equation (4) may be summed over the rotational spectrum to obtain the integrated band absorption coefficient,

$$\int_{v'v''} \mu_{\nu} d\tilde{\nu} = \pi r_0 f_{v'v''} N_{v''} \quad (5)$$

where $f_{v'v''}$ is related to the electronic dipole matrix element for the transition,

$$R_{v'v''} = \int \Psi_{v'} M \Psi_{v''} d\tau, \quad (6)$$

by the equation

$$f_{v'v''} = \left(\frac{\tilde{\nu}}{3R_{\infty}} \right) \left| \frac{R_{v'v''}}{ea_0} \right|^2 \quad (7)$$

where R_{∞} is the Rydberg and a_0 is the radius of the first Bohr orbit.

It has been shown by FRASER⁽²⁾ that, under a variety of practical conditions, $|R_{v'v''}|^2$ may be approximately expressed

$$|R_{v'v''}|^2 = R^2(\bar{r}) q_{v'v''} \quad (8)$$

where

$$\bar{r} = \int \phi_{v'} r \phi_{v''} d\tau \quad (9)$$

is the r -centroid and

$$q_{v'v''} = \left| \int \phi_{v'} \phi_{v''} d\tau \right|^2 \quad (10)$$

is the Franck-Condon factor for which the sum rule

$$\sum_{v'} q_{v'v''} = \sum_{v''} q_{vv''} = 1 \quad (11)$$

applies. In equations (9) and (10), $\phi_{v'}$ and $\phi_{v''}$ are the vibrational wave functions for the levels involved in the transition. Combining equations (5), (7) and (8), we obtain

$$\int_{\tilde{\nu}''} \mu_{\nu} d\tilde{\nu} = \pi r_0 \left(\frac{\tilde{\nu}}{3R_{\infty}} \right) \left(\frac{R(\bar{r})}{ea_0} \right)^2 q_{vv''} N_{v''}. \quad (12)$$

Thus, if values of $q_{v'v''}$ can be calculated, measurements of the integrated band absorption coefficient can be used to calculate $R(\bar{r})$.

A second method of determining $R(\bar{r})$ is to sum equation (12) over all values of v' , including those in the continuum. This procedure leads to the equation

$$\sum_{v'} \int_{\tilde{\nu}''} \mu_{\nu} d\tilde{\nu} + \int \mu_{\nu} d\tilde{\nu} = \pi r_0 \left(\frac{\tilde{\nu}_a}{3R_{\infty}} \right) \left(\frac{R(\bar{r})}{ea_0} \right)^2 N_{v''} \quad (13)$$

where

$$\tilde{\nu}_a = \sum_{v'} \tilde{\nu} q_{v'v''} + \int \tilde{\nu} q(\tilde{\nu} v'') d\tilde{\nu}. \quad (14)$$

Equation (13) may be used to determine $R(\bar{r})$ from measurements of the total integrated absorption coefficient for a given v'' level. This method has the advantage over the preceding one that it does not depend in a sensitive way on the precise determination of the $q_{v'v''}$ values which enter only in the definition of $\tilde{\nu}_a$. It has the disadvantage that it cannot be applied in cases where $R(\bar{r})$ changes appreciably in the interval over which the absorption is important.

For cases where the absorption associated with a given electronic transition is due to many overlapping bands, as it is at high temperatures, a third method may be used to determine $R(\bar{r})$. This involves summing equation (1) over all lines falling in a small frequency interval $\Delta\tilde{\nu}$ and dividing by $\Delta\tilde{\nu}$ to obtain the "average" absorption coefficient $\bar{\mu}$.

A convenient form of the result is: (3,4)

$$\bar{\mu} = \pi r_0 \left(\frac{\tilde{\nu}}{3R_{\infty}} \right) \left(\frac{R(\bar{r})}{ea_0} \right)^2 N \phi \frac{hc}{kT} \left[\exp - \frac{hc}{kT} (\tilde{\nu}_{00} - \tilde{\nu}) \right] \quad (15)$$

where

$$\phi = \frac{kT}{hc} \frac{1}{Q''_v Q''_r (B'_e - B''_e)} \sum_{\epsilon'_v \geq 0} q_{v'v''} \exp[-(\epsilon'_v + \epsilon'_r)/kT] \quad (16)$$

is a dimensionless factor giving the details of the vibrational spectrum. In equation (15) and (16), N is the concentration of absorbing molecules, Q''_v and Q''_r are the vibrational and rotational partition functions for the absorbing molecules, B'_e and B''_e are the rotational constants for the upper and lower electronic states, and ϵ'_v and ϵ'_r are vibrational and rotational energies of the upper state. In deriving equation (15), the assumption has been made that the detailed rotational structure may be described by the expression

appropriate for a Q branch. It, therefore, does not give correctly the details of the spectrum within an interval $\Delta\tilde{\nu} \sim B_e^2/\Delta B_e$ of the band head, but is a reasonable approximation elsewhere. Equations (15) and (16) are the basic equations determining the emissivity of air and may be used to determine the value of $R(\tilde{\nu})$ as a function of $\tilde{\nu}$ in much the same manner that Nicholls has determined $R(\tilde{\nu})$ as a function of $\tilde{\nu}$ from integrated band intensity measurements. It may be noted that, to the extent that $\tilde{\nu}$ is only a function $\tilde{\nu}$, the methods are completely equivalent.

The final method of determining $R(\tilde{\nu})$ is to use the Einstein relation between the spontaneous and induced emission coefficients. This leads to an expression for the lifetime τ of an excited electronic level which may be conveniently written

$$\frac{1}{\tau} = \frac{8\pi^2 r_0 c \tilde{\nu}_e^3}{3R_\infty} \frac{g''}{g'} \left(\frac{R(\tilde{\nu})}{ea_0} \right)^2 \quad (17)$$

where g' and g'' are the electronic degeneracies of the upper and lower states, respectively, and

$$\tilde{\nu}_e^3 = \sum_{v''} \tilde{\nu}^3 q_{v''v''}. \quad (18)$$

In deriving equation (17), the assumption has again been made that $R(\tilde{\nu})$ is independent of $\tilde{\nu}$. Equation (17) may be used to determine $R(\tilde{\nu})$ from measurements of life times of excited molecular states. The inherent precision of this method of determining $R(\tilde{\nu})$ is probably greater than that of any of the other methods discussed provided that the possibility of the excited state under study being populated by cascading from above is eliminated.

A. Kramers' radiation from neutrals

The only important free bound radiation which must be considered in the temperature range from 4000 to 9000°K is that associated with capture of electrons by O atoms. This radiation may be calculated most simply from the measurements of the photodetachment cross-section reported by BRANSCOMB and SMITH^(5,6) using the simple formula

$$\frac{dI}{dV d\Omega d\tilde{\nu}} = \sigma 2hc^2 \tilde{\nu}^3 [\text{O}^-] \exp\left(-\frac{hc\tilde{\nu}}{kT}\right) \quad (19)$$

which is obtained from detailed balance.

There are two types of electronic scattering processes responsible for radiation from ionized gases—scattering from ions (coulombic fields) and scattering from neutrals. Calculations indicate that the latter process dominates in air and nitrogen up to temperatures around 10,000°K, and hence coulombic scattering will be omitted from the present study. A simple treatment of the free-free radiation associated with scattering of electrons by neutrals has not yet been given. We shall, therefore, assume that this component of radiation may be approximately described by the classic Kramers' formula⁽⁷⁾

$$\frac{dI}{dV d\Omega d\tilde{\nu}} = Z^2 \frac{16\pi}{3\sqrt{3}} \frac{e^6}{mc^2} \frac{[N][e]}{(2\pi mkT)^{1/2}} \exp\left(-\frac{hc\tilde{\nu}}{kT}\right) \quad (20)$$

with the effective Z^2 being determined from experiment; $[N]$ is the concentration of

neutrals doing the scattering. If there is more than one neutral species effective in scattering, then each species contributes a term like equation (20), with its own effective Z^2 , to the total radiation.

B. Franck-Condon factors

The reduction of the experimental results to electronic transition moments requires a knowledge of the Franck-Condon factors $q_{v'v''}$ and r -centroids, $\bar{r}_{v'v''}$. A summary of the various calculations which have been made of these quantities for air bands is given in Table 1. The most extensive work has been that carried out by Nicholls, Fraser, Jarman and co-workers who have used Morse wave functions in computing the integrals in equations (9) and (10). In addition, $q_{v'v''}$ values for NO(β) and NO(γ) bands have been computed by KIVEL *et al.*⁽⁹⁾ using modified harmonic oscillator wave functions and by FLINN *et al.*⁽¹⁴⁾ using wave functions for potential curves determined from spectroscopic data by the Rydberg-Klein-Rees method. Finally, CHILDS⁽¹⁹⁾ has devised a recursion method for calculating $q_{v'v''}$ values for Morse wave functions which is very efficient but requires high numerical accuracy.

TABLE 1. SUMMARY OF CALCULATIONS OF FRANCK-CONDON FACTORS, $q_{v'v''}$ AND r -CENTROIDS, $\bar{r}_{v'v''}$ FOR AIR BANDS

Numbers refer to references. The * denotes the reference used in the present analysis.

Band	$\bar{r}_{v'v''}$	$q_{v'v''}$
O ₂ (SR)	(8)*	(10) (11) (12)* (19)
NO(β)	(9)* (16)*	(9) (11) (13)* (14) (19)
NO(γ)	(8)*	(9) (13)* (14) (15) (19)
N ₂ (1 +)	(8)*	(15) (17) (18)* (19)
N ₂ (2 +)	(8)*	(15) (17) (18)* (19)
N ₂ (1 -)	(8)*	(10) (15) (18)* (19)

An interesting comparison, which exhibits the sensitivity of these calculations to the exact form of the potential used, is shown in Fig. 1 for the NO(β) bands which are important in absorption at room temperature. These bands, which lie well outside the Condon parabola, have $q_{v'v''}$ values which are relatively small, and it can be seen that the various calculations differ from one another by factors of two. We are thus led to conclude that one cannot rely too heavily on calculations involving $q_{v'v''}$ values which are very small. This conclusion is of particular importance in the interpretation of room temperature absorption measurements of the O₂ (Schumann-Runge) and NO(β) bands.

III. ELECTRONIC TRANSITION MOMENTS

The emission and absorption spectrum of air in the temperature range from 4000 to 9000°K is determined primarily by radiation from the six molecular bands: O₂(SR), NO(β), NO(γ), N₂(1 +), N₂(2 +) and N₂⁺(1 -). There is also a significant contribution due to Kramers' radiation from electrons scattered and captured by O, N and N₂.

We have reviewed the available experimental data relating to these systems and used them in conjunction with the equations given in section II and the Franck-Condon factors given in references (12), (13) and (18) to determine appropriate $(R/ea_0)^2$ and

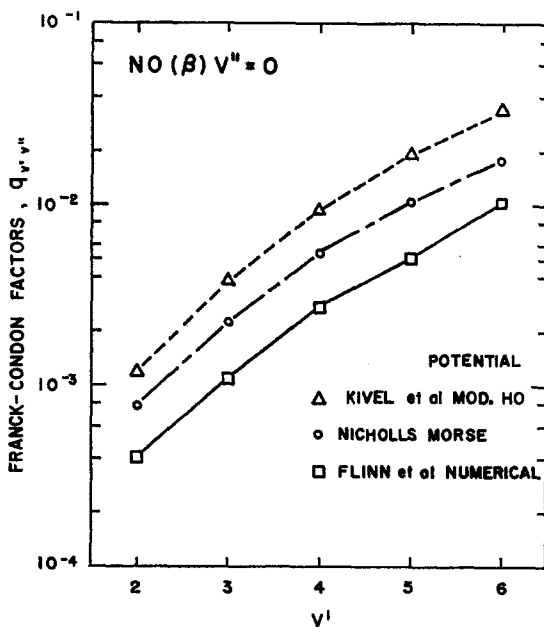


FIG. 1. Comparison of Franck-Condon factors $q_{v'v''}$ for the NO(β) bands important in room temperature absorption experiments computed by KIVEL *et al.*⁽⁹⁾ for a modified harmonic oscillator potential, NICHOLLS⁽¹³⁾ for a Morse potential and FLINN *et al.*⁽¹⁴⁾ for a potential determined from spectroscopic data by the Rydberg-Klein-Rees method.

effective Z^2 values. The results for the molecular bands are presented in Figs. 2 through 7 which show $(R/ea_0)^2$ values plotted as a function of the r -centroid, $\bar{r}$, obtained from references (8), (9) and (16). Also shown in the upper part of the figures is a curve of wavelength, λ , (left scale) and wavenumber, $\tilde{\nu}$, (right scale) as a function of $\bar{r}$. The number pairs along the curve refer to $v'v''$ transitions and the wavenumbers $\tilde{\nu}_a$ and $\tilde{\nu}_e$ are those defined in equations (14) and (18). The results for the free-free Kramers' radiation are given in Fig. 9 which presents the effective Z^2 values along with a comparison of theory and experimental data.

A. O₂ Schumann-Runge bands

The integrated absorption coefficient for the O₂ Schumann-Runge continuum has been measured at room temperature by LANDENBURG and VAN VOORHIS,⁽²⁰⁾ DITCHBURN and HEDDLE⁽²¹⁾ and WATANABE *et al.*⁽²²⁾ $(R/ea_0)^2$ values obtained from their data using equation (13) are shown in Fig. 2. To arrive at the values given, we have added to their continuum f -numbers the band absorption sum of 0.00031 obtained by Bethke and subtracted a contribution of 0.01 estimated by WILKINSON and MULLIKEN⁽²³⁾ for the underlying $X^3\Sigma_g^- \rightarrow ^3\Pi_u$ continuum. These corrections amount to less than 10 per cent and the agreement between the different determinations is good.

The integrated band absorption coefficients of O₂(SR) have been measured at room temperature for a number of bands connecting with the ground vibrational level by

BETHKE⁽²⁴⁾ using photometric techniques and by DITCHBURN and HEDDLE⁽²⁵⁾ using photographic techniques. Values of $(R/ea_0)^2$ deduced from Bethke's measurements and using equation (12) are shown in Fig. 2. The corresponding f -values are a factor of two lower than those given by Bethke due to the fact that the $q_{v'v''}$ used⁽¹²⁾ are a factor of two higher than the values⁽¹¹⁾ used by Bethke. It may be noted that the $q_{v'v''}$ factors involved in the transitions measured by Bethke are of the order of 10^{-7} to 10^{-5} and are extremely sensitive to the shape of the repulsive part of the potential. The marked variation of $(R/ea_0)^2$ with $\bar{r}$ is undoubtedly associated with the fact that the Morse curve is not a good approximation to this part of the potential and leaves some doubt as to the reliability of the values determined from Bethke's measurements. The measurements of Ditchburn and Heddle lead to values of $(R/ea_0)^2$ approximately 100 times Bethke's and it has been acknowledged by Heddle that they are probably in error.⁽²⁶⁾

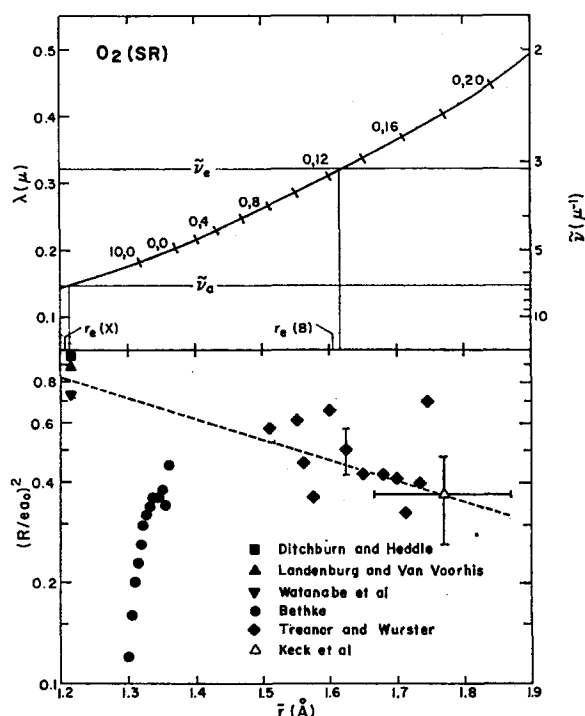


FIG. 2. Wavelength, λ , frequency, $\bar{\nu}$, and electronic transition probability, $(R/ea_0)^2$, as a function of the r -centroid, $\bar{r}$, for the Schumann-Runge bands of O_2 .

Measurements similar to Bethke's for a number of bands important in emission have been made at high temperature (3000°K) in a shock tube by TREANOR and WURSTER⁽²⁷⁾ and values of $(R/ea_0)^2$ deduced from their data are also shown in Fig. 2. Their measurements, although inherently less precise than those of Bethke due to the difficulty of determining conditions in a shock tube with precision, have the important advantage that the associated $q_{v'v''}$ are of the order of 10^{-1} and thus cannot be appreciably in error.

Finally, measurements of the emissivity of O_2 at high temperatures (4000°K) have been

made in shock tubes by KECK *et al.*⁽³⁾ in the wavelength region 3300 to 4700 Å. The average $(R/ea_0)^2$ value deduced using equation (15) from these measurements is in excellent agreement with Treanor and Wurster's values.

The general trend of the data suggests that $(R/ea_0)^2$ decreases with increasing $\bar{r}$, which is reasonable since the transition involved is forbidden for the separated atoms. A good fit to the data is given by the expression

$$\left(\frac{R}{ea_0}\right)^2 = 0.47 \exp[-1.43 (\bar{r} - 1.60)], \quad 1.2 < \bar{r} < 1.9 \text{ Å}, \quad (21)$$

which produces the dashed curve in Fig. 2. In making this fit, we have not weighed Bethke's data heavily because of the relatively large uncertainty which it is felt exists in the corresponding $q_{v'v''}$ values. Because of this, however, one cannot expect to reconstruct the absorption coefficient for these bands from equation (15). This observation is of little consequence for emission studies because these bands radiate so weakly, but it could be important in absorption studies.

B. NO(γ) bands

Absolute measurements of the integrated band absorption coefficient for the most important NO(γ) bands have been made at room temperature by WEBER and PENNER⁽²⁸⁾

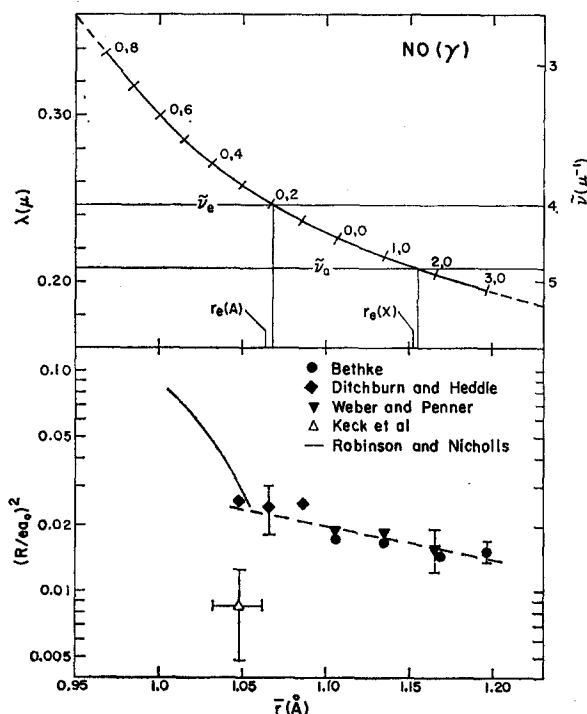


FIG. 3. Wavelength, λ , frequency, $\tilde{\nu}$, and electronic transition probability, $(R/ea_0)^2$, as a function of the r -centroid, $\bar{r}$, for the gamma bands of NO.

and by BETHKE⁽²⁹⁾ and at high temperatures (2000°K) in a shock tube by DAIBER and WILLIAMS.⁽³⁰⁾ The $(R/ea_0)^2$ values deduced from their data using equation (12) are shown in Fig. 3. The agreement between various workers is excellent and the data are well described by the expression.

$$\left(\frac{R}{ea_0}\right)^2 = 0.022 \exp[-3.5(\bar{r} - 1.07)], \quad 1.04 < \bar{r} < 1.20 \text{ \AA}, \quad (22)$$

which produces the dashed curve in Fig. 3.

The solid curve in the figure is proportional to $(1 - 0.899\bar{r})^2$, which represents the variation in $(R/ea_0)^2$ found for the interval $1.01 < \bar{r} < 1.06 \text{ \AA}$ by ROBINSON and NICHOLLS⁽¹⁶⁾ from relative intensity measurements. The curve has been arbitrarily normalized to the data of DAIBER and WILLIAMS.⁽³⁰⁾ In this case, as in the case of Bethke's O₂ data, it is felt that the steep variation is due to the failure of the Morse curve to represent the repulsive part of the potential and does not reflect the true variation of $(R/ea_0)^2$.

A value of $(R/ea_0)^2$ deduced from emissivity measurements for shock-heated air at 8000°K by KECK *et al.*⁽³⁾ using equation (15) is also shown in Fig. 3. Under the conditions of measurements the NO(γ) bands accounted for less than a third of the total emission from air and the reliability of this measurement is therefore very low. It has been given no weight in fitting the curve of equation (22) to the data.

C. NO(β) bands

The integrated absorption coefficients for several bands of the NO(β) system have been measured by BETHKE⁽²⁹⁾ at room temperature, and the $(R/ea_0)^2$ values deduced from equation (12) are given in Fig. 4. It should be noted that there is considerable uncertainty in these values due to the fact that the corresponding $q_{v'v''}$ values shown in Fig. 1 for various potential curves differ by factors of two. In the present analysis, we have used the values computed by NICHOLLS⁽¹³⁾ for a Morse curve. Had we used those of FLINN *et al.*⁽¹⁴⁾ which, in principle, should be better, Bethke's points would be raised by a factor of two.

Fortunately, a reasonably good value for $(R/ea_0)^2$ for the NO(β) bands in emission may be obtained from the shock tube measurements of KECK *et al.*⁽³⁾ The NO(β) bands are responsible for almost all of the radiation from air in the quartz ultraviolet and, although no identifiable structure can be seen, excellent agreement with the theoretical temperature and density dependence of this band system was obtained over a wide range of conditions for both incident and reflected shocks. The analysis was carried out using equation (15).

The best indication of the variation of $(R/ea_0)^2$ with $\bar{r}$ is given in this case by the relative intensity measurement of ROBINSON and NICHOLLS⁽¹⁶⁾ who fit an equation of the form $R = \text{const} (1.607\bar{r} - 1)$ to their data in the range $1.33 < \bar{r} < 1.50 \text{ \AA}$. Normalizing their equation to fit the shock tube results we obtain

$$\left(\frac{R}{ea_0}\right)^2 = 0.10 (\bar{r} - 0.62)^2, \quad 1.33 < \bar{r} < 1.54 \text{ \AA}, \quad (23)$$

which produces the solid curve in Fig. 4.

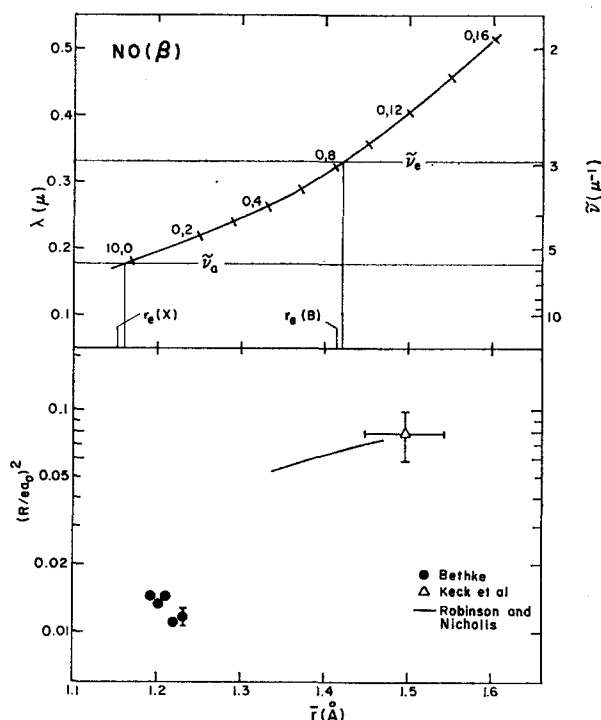


FIG. 4. Wavelength, λ , frequency, $\bar{\nu}$, and electronic transition probability, $(R/ea_0)^2$, as a function of the r -centroid, $\bar{r}$, for the beta bands of NO.

D. $N_2^+(1-)$ bands

The radiative life-times for several $N_2^+(1-)$ bands have been measured by BENNETT and DALBY⁽³¹⁾ and the corresponding $(R/ea_0)^2$ value computed from equation (12) is shown in Fig. 5. Except for the possibility that the upper state is being populated by cascading from higher states, which would increase the apparent life-time, this measurement should be very good.

Measurements of the emitted radiation from this system have also been made for shock-heated N_2 by ALLEN *et al.*⁽³²⁾ and for air by KECK *et al.*⁽³⁾ from which values of $(R/ea_0)^2$ have been determined using equation (15). As can be seen in Fig. 5, these values lie somewhat above Bennett and Dalby's value, but the precision of the measurements is relatively low, due to the extremely strong temperature dependence of the radiation from this system. The fractional error in $(R/ea_0)^2$ is roughly 30 times the fractional error in the temperature. This effect is particularly serious in the case of the measurements by KECK *et al.*,⁽³⁾ which were made behind strongly accelerating reflected shock waves. Due to the complicated flow behind reflected shocks associated with the boundary layer-shock wave interaction, it has not been possible to estimate the magnitude of the effect. However, it almost certainly results in a temperature higher than that calculated by Keck and his co-workers, and thus their measurements must for the present be regarded as giving an upper bound to $(R/ea_0)^2$. There has been some concern that CN may be contributing to the radiation observed in the experiments of KECK *et al.*, but this

possibility can be ruled out on the basis of the strong temperature dependence of the observed radiation. Under the conditions of measurement, one can expect that any CN is in equilibrium with CO and the CO will tie-up most of the carbon. The intensity of the CN radiation is thus proportional to $\exp \{-(D_{\text{CO}} - D_{\text{CN}} + h\nu_{00})/kT\} \sim \exp \{-60,000/T\}$ which is to be compared to $\exp \{-200,000/T\}$ for the observed radiation.

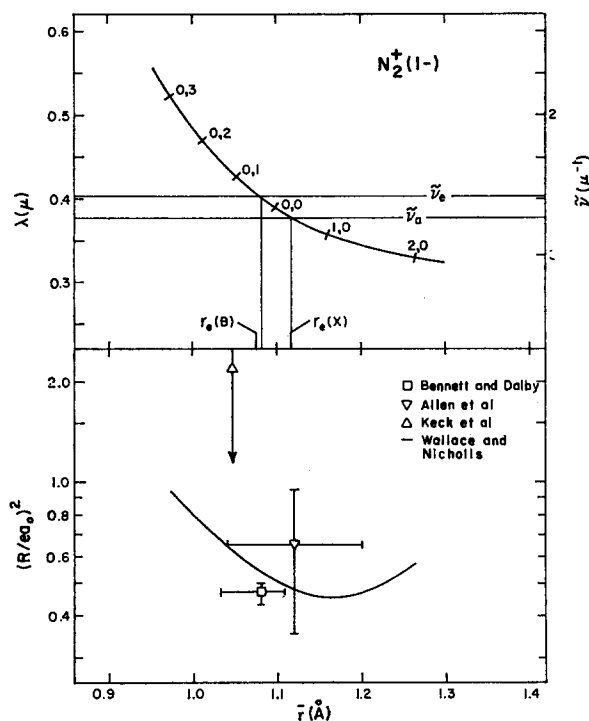


FIG. 5. Wavelength, λ , frequency, $\tilde{\nu}$, and electronic transition probability, $(R/ea_0)^2$, as a function of the r -centroid, $\bar{r}$, for the first negative bands of N_2^+ .

Finally, relative intensity measurements of the integrated intensities of a number of $\text{N}_2^+(1-)$ bands have been made by WALLACE and NICHOLLS⁽³³⁾ who fit their data with an equation of the form $R = \text{const} (0.697\bar{r}^2 - 1.62\bar{r} + 1)$ for $0.974 < \bar{r} < 1.265 \text{ \AA}$. It is to be noted that there is apparently an error in the sign of the last term in equation (6) of Wallace and Nicholls' paper and that the equation given here is the one which fits the data.

Using the corrected equation and normalizing to fit the data of BENNETT and DALBY⁽³¹⁾ and ALLEN *et al.*,⁽³²⁾ we obtain the expression

$$\left(\frac{R}{ea_0}\right)^2 = 0.45 [1 + 12.3 (\bar{r} - 1.16)^2], \quad 0.97 < \bar{r} < 1.26 \text{ \AA}, \quad (24)$$

which produces the solid curve in Fig. 5. In weighing the measurements of Bennett and

Dalby, we have made a small allowance for the possibility of systematic error due to cascading.

E. $N_2(2+)$ bands

Measurements of the radiative life-time of two $N_2(2+)$ bands have been made by BENNETT and DALBY⁽³¹⁾ and the corresponding $(R/ea_0)^2$ value is shown in Fig. 6. For this band system, they reported definite evidence of cascading, and the measurement is not as precise as that for the $N_2^+(1-)$ system.

The intensity of the radiation from this band system may be deduced from the measurements of KECK *et al.*⁽³⁾ in shock-heated air in the wavelength region 2900 to 3400 Å. The corresponding value of $(R/ea_0)^2$ shown in Fig. 6 was computed from equation (15). As in the case of the $N_2^+(1-)$, the main source of error in the shock tube measurements is the determination of the temperature behind the accelerating reflected waves

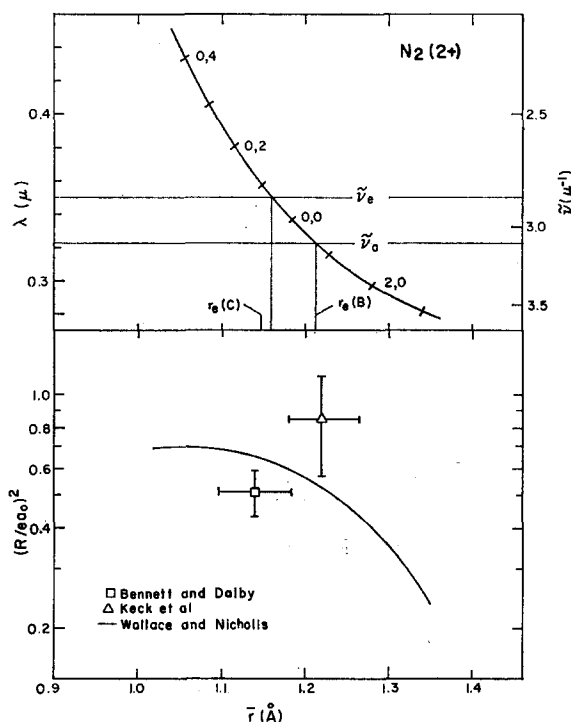


FIG. 6. Wavelength, λ , frequency, $\tilde{\nu}$, and electronic transition probability, $(R/ea_0)^2$, as a function of the r -centroid, $\bar{r}$, for the second positive bands of N_2 .

employed, and, for this reason, the value of $(R/ea_0)^2$ is more likely to be high than low. Since Bennett and Dalby's value of $(R/ea_0)^2$ is more likely to be low than high, there is a good chance that the true value lies between these two determinants.

Relative integrated intensity measurements for a number of bands of the $N_2(2+)$ system have been made by WALLACE and NICHOLLS⁽³³⁾ who fit their data with an equation

of the form $R = \text{const} (1.102 \bar{r}^2 - 2.32 \bar{r} + 1)$ in the interval $1.02 < \bar{r} < 1.35 \text{ \AA}$. Normalizing this equation to fit the data of Bennett and Dalby and Keck *et al.*, we obtain the expression.

$$\left(\frac{R}{ea_0}\right)^2 = 0.7 [1 - 4.9(\bar{r} - 1.06)^2], \quad 1.02 < \bar{r} < 1.35 \text{ \AA}, \quad (25)$$

which produces the solid curve in Fig. 6.

F. $\text{N}_2(1+)$ bands

The only available data on which we may base an estimate of the absolute value of $(R/ea_0)^2$ for $\text{N}_2(1+)$ band system come from measurements of the emitted radiation from shock-heated N_2 and air in the wavelength range $0.55 < \lambda < 1.4 \mu$.

Measurements of the radiation from shock-heated N_2 have been made by WURSTER⁽³⁴⁾ using reflected shock waves and by ALLEN *et al.*⁽³²⁾ using incident shock waves. The $(R/ea_0)^2$ values computed from their data using equation (15) are shown in Fig. 7. Each of the points represents the mean of several measurements at a given wavelength and the scatter shown is roughly indicative of the scatter in the original data. In our analysis of Wurster's data, we have eliminated all those points where there was any possibility of serious interference from the CN (red) system.

Relative intensity measurements have been made for this band system by TURNER and NICHOLLS⁽³⁵⁾ who fit their data with an equation of the form $R = \text{const.} \exp(-3.02 \bar{r})$ over the interval, $1.17 < \bar{r} < 1.59 \text{ \AA}$. This expression, normalized to give the best fit to all of the data, gives the equation,

$$\left(\frac{R}{ea_0}\right)^2 = 0.21 \exp[-6.04(\bar{r} - 1.23)], \quad 1.17 < \bar{r} < 1.59 \text{ \AA}, \quad (26)$$

which produces the solid line in Fig. 7. Although Wurster claims in his paper that no significant variation of R with $\bar{r}$ was observed, it appears from our analysis that there is in fact a variation of R in both Wurster's and Allen and co-worker's data which is compatible with that found by Turner and Nicholls for a much wider range of $\bar{r}$. If we assume the variation given by Turner and Nicholls is correct, then Wurster's data are found to be a factor of two lower than that of Allen *et al.* This discrepancy is equivalent to a 300°K difference in temperature, and a possible source of error could lie in the methods used to calculate the temperature behind the shock waves. However, we have cross-checked our calculations with those used by Wurster and find virtually perfect agreement. The only remaining possibility which seems reasonable is that the effect is in some way associated with the fact that Wurster used reflected shocks produced by pressure driven incident shocks, while Allen *et al.* used combustion driven incident shocks.

A much more important effect than the relatively small discrepancy just discussed is the dramatic increase in the radiation in the region of the $\text{N}_2(1+)$ bands which has been observed for reflected shock waves in air by Wurster *et al.*⁽³⁶⁾ The situation is shown in Fig. 8, where we have plotted their data for 6300°K in air along with the related data of WENTINK *et al.*⁽³⁷⁾ and KECK *et al.*⁽³⁾ for 8000°K air, and Wurster and Allen *et al.* for pure N_2 . The data have all been normalized to the same temperature and partial nitrogen density on the assumption that the only radiation in this region of the spectrum is due to $\text{N}_2(1+)$

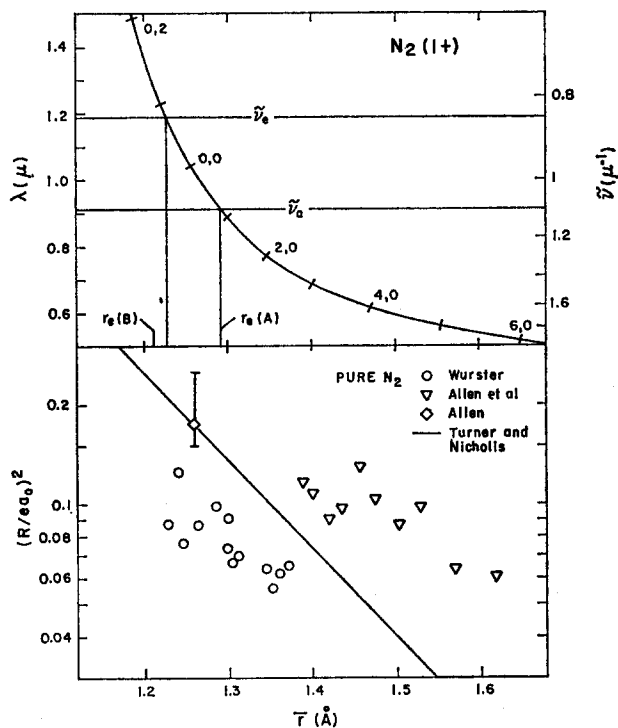


FIG. 7. Wavelength, λ , frequency, $\tilde{\nu}$, and electronic transition probability, $(R/ea_0)^2$, as a function of the r -centroid, $\bar{r}$, for the first positive bands of N_2 .

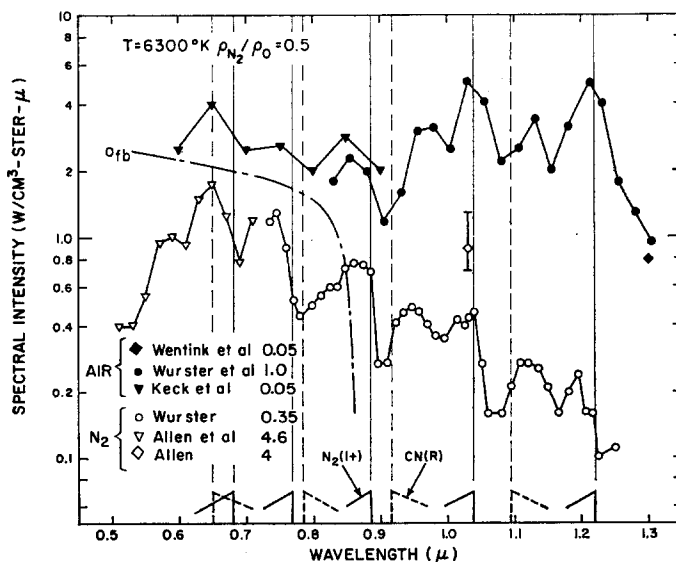


FIG. 8. Comparison of infrared spectra obtained by WENTINK *et al.*⁽³⁷⁾ WURSTER *et al.*⁽³⁶⁾ KECK *et al.*⁽³⁾ for air heated by reflected shock waves, by WURSTER⁽³⁴⁾ for N_2 heated by reflected shock waves and by ALLEN *et al.*⁽³²⁾ for N_2 heated by incident shock waves.

bands and Kramers' radiation from neutrals (discussed below). The multiplication factors involved in each case are given in the figure following the author identification. In general, the agreement between various workers is fairly good in the limited regions of overlap, particularly for the air data. In the wavelength region from 0.5 to 0.85 μ the air radiation can be reasonably accounted for as a superposition of N₂(1+) bands and free-bound radiation from capture of electrons by O atoms.

In the wavelength region beyond the O_{fb}⁻ edge at 0.86 μ , however, the air radiation is an order of magnitude larger than that expected for the N₂(1+) bands on the basis of Wurster's measurements. This has led Wurster *et al.* to suggest the possibility that the additional radiation is due to some as yet unidentified bands of NO. The remarkable thing about this additional radiation is that it exhibits practically the same gross structure as the radiation from pure N₂ which Wurster reasonably attributes to an overlapping of N₂(1+) and CN (red) bands. There is certainly a difference in the overall trend with wavelength and, in a private communication, Treanor has pointed to a number of differences in structural detail, but the fact remains that the major features of the N₂ spectrum are all reproduced in the air spectrum to a degree which becomes even more impressive if one notes that the CN contributions in air shocks should be somewhat suppressed due to the formation of CO.

In addition to the spectral measurement reproduced in Fig. 8, Wurster *et al.* have measured the temperature dependence of the air radiation at wavelengths of 1.04 and 1.219 μ over the range 5500 to 6700°K. While they have interpreted their results to give activation energies for the upper states of the proposed NO bands, one can equally well interpret the data as due to N₂(1+) bands overlapped by a small component of Kramers' radiation from neutrals.

The most convincing evidence put forward by Wurster *et al.* in support of the NO band hypothesis is a plot of the radiation as a function of NO concentration obtained by varying the N₂ to O₂ ratio of the shocked gas. Unfortunately, these measurements were made at a somewhat lower temperature (5000°K) than the other measurements in a region where the free-free Kramers' radiation from neutrals and NO₂ radiation become relatively more important. Since the radiation from both these sources will be correlated with the NO concentration, this could also explain the observations.

In the light of the above considerations, the evidence for the NO band hypothesis is not completely convincing. Unfortunately, we have no alternative to offer except to suggest the possibility of quenching of the N₂(1+) bands in the N₂ shocks by some unknown mechanism, possibly CN. In any case, we feel that this is a matter requiring further study.

In the interim, we suggest that for practical purposes, the radiation from air in the near infrared can best be described by assuming an "effective"

$$\left(\frac{R}{ea_0}\right)^2 = 0.8 \exp[-6.04(\bar{r}-1.23)], \quad 1.17 < \bar{r} < 1.59 \text{ \AA}, \quad (27)$$

for the N₂(1+) bands radiating in shock-heated air.

IV. KRAMERS' RADIATION

No direct measurement of the free-bound Kramers' radiation from electrons captured by O-atoms has yet been made. The procedure, which has been universally adopted

for calculating this radiation, is to use the photo-detachment cross-sections for O—measured by BRANSCOMB and SMITH⁽⁵⁾ in conjunction with equation (19). Techniques for extrapolating the measured cross-sections to higher energies differ somewhat, but we are inclined to favor the procedure used by Kivel based on work by KLEIN and BRUECKNER⁽³⁸⁾ and presented in Fig. 22 of KECK *et al.*⁽³⁾

Studies of the free-free Kramers' radiation from shock-heated air at 8000°K have been made by WENTINK *et al.*⁽³⁷⁾ and from shock-heated air and N₂ from 6000 to 9000°K by TAYLOR.⁽³⁹⁾ Taylor has recently analyzed his data on the temperature dependence of the radiation to obtain effective Z^2 values for O, N and N₂. The technique involves using the equation

$$\frac{dI}{dV d\Omega d\nu} = k(\tilde{\nu}, T) [e] \left[Z_N^2 [N] + Z_{N_2}^2 [N_2] + Z_O^2 [O] \right],$$

where $k(\tilde{\nu}, T)$ includes the wavelength and temperature dependent factors of equation (20), to make a simultaneous least squares fit of the intensity measurements for shock-heated N₂ and air from 6000 to 9000°K in the wavelength region 2.35 to 3.88 μ .

Over this temperature range, there is appreciable change in the relative concentrations of the various atomic and molecular species which allows a determination of the effective Z^2 for each species. Note that for air under these conditions, the contribution to the radiation from scattering of electrons by NO and O₂ can be neglected because of the small concentration of these molecules.

The results are given in Fig. 9, which shows a comparison of the experimental data for

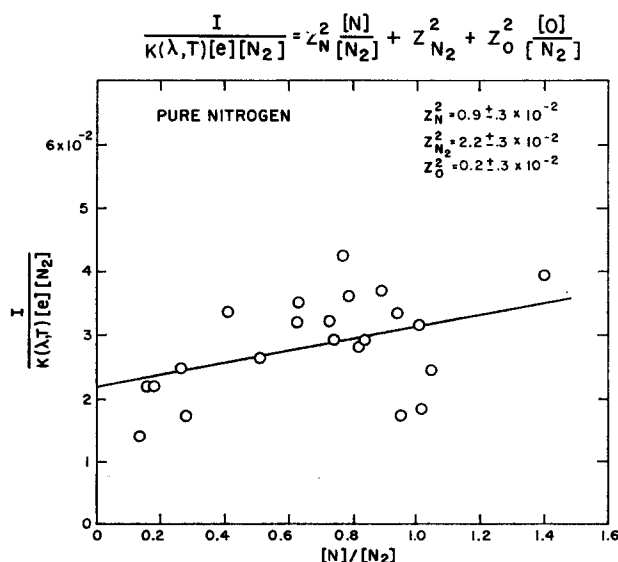


FIG. 9. Dimensionless intensity of the infrared radiation from shock heated N₂ at 3.07 μ wavelength over the temperature range of 6000–9000°K as a function of the [N] to [N₂] ratio showing fit of theoretical Kramers' formula to the experimental data. The intercept of the formula gives $Z_{N_2}^2$ while the slope yields Z_N^2 .

pure N₂ with the fitted curve. A complete report on this work will be published shortly by Taylor.

It should be noted that this work changes considerably the interpretation of the free-free continuum from air which has been made in the past.⁽³⁷⁾ This radiation which was previously associated almost entirely with scattering from O-atoms now appears to be due mostly to scattering from N₂ and N with O giving a negligible contribution.

V. EMISSIVITY TABLES FOR AIR

Extensive tables of the emissivity of high temperature air based on the measurements reviewed above have been prepared by MEYEROTT,⁽⁴⁰⁾ KIVEL and BAILEY⁽⁴¹⁾ MEYEROTT *et al.*,⁽⁴²⁾ BREEN and NARDONE,^(43,44) and BREENE, *et al.*⁽⁴⁵⁾ Unfortunately space has not permitted us to review all of these tables in detail but, in general, the predicted values of the total air radiation in the interval from 4000 to 9000°K agree with the shock tube measurements of KECK *et al.*⁽³⁾ and WURSTER *et al.*⁽³⁶⁾ to within a factor of two or three. None of them can be regarded as completely satisfactory, however, and it would appear that significant improvements could and should be made. In this connection, we should like to call attention to a number of errors which have been found in the work of Breene and Nardone and co-workers. In so doing, we do not wish to create the impression that their work necessarily gives a less accurate representation of the air radiation than other work, but, since it is the most recent and ambitious, we feel that prospective users of their tables should be aware of the potential difficulties: (1) In treating the O₂ (SR) bands, Breene and Nardone have used a formula $R(\bar{r}) = \text{const.} (0.897 \bar{r}^2 + 2.416 \bar{r} - 1)$ obtained by NICHOLLS⁽⁴⁶⁾ from an analysis of the data of Ditchburn and Heddle. Since Ditchburn and Heddle's work is now found to be in serious error, we cannot accept Nicholls' analysis either. In addition, there appears to be an error in the equation given by Nicholls in that it does not agree with the curve drawn through the experimental points in Fig. 4 of his paper. (2) In treating the NO (γ) bands, Breene and Nardone have used the equation $R(\bar{r}) = \text{const.} (1 - 0.899\bar{r})$ given by ROBINSON and NICHOLLS⁽¹⁶⁾ as representing the variation of $R(\bar{r})$ in the interval $1.01 < \bar{r} < 1.06$ Å. As can be seen in Fig. 3 of this paper, this relation is not all satisfactory outside of this interval and, in fact, has a zero at $\bar{r} = 1.11$ Å which would imply nearly zero intensity for the (0,0) band. (3) In treating the NO (β) bands, Breene and Nardone have based their f -number on an analysis of BETHKE's⁽²⁹⁾ absorption measurements using $q_{v'v''}$ values computed by KIVEL *et al.*⁽⁹⁾ As can be seen in Fig. 1 of this paper, there is considerable uncertainty in these $q_{v'v''}$ values and it is doubtful if they can be relied on even to a factor of three. (4) In treating the N₂⁺(1-) bands, Breene and Nardone have used the equation $R(\bar{r}) = \text{const.} (0.697\bar{r}^2 - 1.62\bar{r} - 1)$ given by WALLACE and NICHOLLS⁽³³⁾ which, as previously noted, contains an error in the relative sign of the last term with respect to the first two terms. (5) In treating the N₂(2+) system, Breene and Nardone have used the equation $R(\bar{r}) = \text{const.} (1.102\bar{r}^2 - 0.232\bar{r} + 1)$ in which a decimal point has apparently been misplaced in the second term. The equation as given by Wallace and Nicholls is $R(\bar{r}) = \text{const.} (1.102\bar{r}^2 - 2.32\bar{r} + 1)$.

It is not clear which of the above errors occur only in the manuscript and which have found their way into the calculations, but the above points should be checked before using the results.

VI. SUMMARY

Electronic transition moments for the molecular bands, which determine the emissivity of air in the temperature range 4000 to 9000°K have been determined from the available experimental data used in conjunction with recently computed Franck-Condon factors. The experimental results are shown in Figs. 2 through 7. Empirical curves which give a reasonable fit to the data are given by equations (21) through (27). For O₂(SR) and NO(γ) the agreement between various determinations is good and the results are felt to be reasonably accurate over the specified range. For NO(β), N₂⁺⁽¹⁻⁾ and N₂(2+), there is insufficient data to permit reliable cross checks, but there are no significant discrepancies in the data which are available. For N₂(1+) the only absolute measurements from which values of $(R/ea_0)^2$ can be determined come from shock tube experiments, and the situation is quite uncertain because measurements made in air show significantly more radiation than those made in pure N₂. The suggestion by WURSTER *et al.*⁽³⁶⁾ that the additional radiation in air may come from NO bands has been critically examined, and found open to question. As a practical expedient, we have, therefore, given two expressions for the $(R/ea_0)^2$ value of the N₂(1+) bands—one for shock-heated N₂ and the other for shock-heated air.

The Kramers' radiation from electrons scattered and captured by neutrals in air and N₂ has also been examined and analyzed to give the following "effective" Z^2 values:

$$\begin{aligned} Z_{N_2}^2 &= (2.2 \pm 0.3) \times 10^{-2}, \\ Z_N^2 &= (0.9 \pm 0.3) \times 10^{-2}, \\ Z_{O_2}^2 &= (0.2 \pm 0.3) \times 10^{-2}. \end{aligned} \quad (28)$$

No significant contributions due to O₂ or NO are expected due to the relatively low concentration of these species under conditions of appreciable electron concentration in high temperature air.

In concluding, we should like to emphasize that in using the $(R/ea_0)^2$ values given in this report to calculate the molecular radiation from air or its component gases, one must use the Franck-Condon factors specified and attempt only limited extrapolations. Similarly, effective Z^2 values for Kramers' radiation are measured at selected wavelengths and extrapolations to other wavelengths can be in error if they do not rest on a firmer theoretical basis than the Kramers' expression. Neither the theory nor the experiments are as yet sufficiently good to be greatly relied upon for extrapolation, and further work particularly on the N₂(1+) bands, the Kramers' radiation from neutrals, and the variation of electronic transition moments with internuclear separation is much to be desired.

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