

## The aeronomic problem of nitrogen oxides

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### ABSTRACT

From consideration of the observational data on atmospheric nitric oxide, it is found that its concentration at any height must be less than  $10^{11}$  cm<sup>-3</sup>. Theoretical deductions from an aeronomic study show that its concentration could be of the order of  $10^8$  cm<sup>-3</sup> (or  $5 \times 10^8$ ) at about 80 km, and  $10^9$  cm<sup>-3</sup> (or  $5 \times 10^9$ ) at about 65 km. At any height below 70 km the nitric oxide concentration must be less than the ozone concentration.

The dissociation of nitrogen molecules involved in nitric oxide formation depends strongly on photo-ionization by ultraviolet or X-ray radiation and subsequent dissociative recombination. The vertical distribution of nitrogen atoms cannot be determined by a dissociation equilibrium, since it is subject to dynamical effects such as diffusion and atmospheric mixing.

Whatever the processes involved in the formation of nitric oxide, its vertical distribution will tend to follow the atmospheric distribution until it becomes dissociated. A departure from photo-equilibrium conditions cannot occur for nitrogen peroxide molecules, for their lifetime in a sunlit atmosphere is very short.

Nitrous oxide seems to play no role in the mesosphere.

In anticipation of the importance attached to the aeronomic problem of nitrogen oxides in the mesosphere and lower thermosphere, various provisional numerical data are presented.

### I. INTRODUCTION

THE aeronomic problem of nitrogen oxides can only be studied on a theoretical basis, for no observational evidence concerning nitrogen oxides in the high atmosphere has been obtained to date.

Nitric oxide was first considered as an important constituent of the high atmosphere by NICOLET (1945). He found there is a possibility that this gas is quite abundant below the transition region in which molecular oxygen is transformed into atomic oxygen. He judged that the nitric oxide molecule could suitably explain the ionization below 100 km, that is, that "The essential phenomenon in region *D* results from NO photo-ionization." He pointed out that this molecule, with an ionization potential of the order of 9.5 eV, is able to absorb solar radiation of  $\lambda 1300$  Å and, in particular, the Lyman- $\alpha$  radiation at  $\lambda 1215.7$  Å, which is very sensitive to solar flares.

Since this mechanism was proposed, BATES and SEATON (1950) have set forth reasons indicating why it is difficult to consider any other acceptable alternatives such as O<sub>2</sub> and Na photo-ionization. WATANABE, MARMO, and INN (1953), after having measured the absorption coefficients of NO, O<sub>2</sub>, and other molecules, concluded that the formation of the *D*-layer by NO as indicated by NICOLET (1945) can be a satisfactory explanation, since L $\alpha$  lies in an atmospheric window. Use of the absorption coefficients of molecular oxygen in the region of its first continuum (WEISSLER and LEE, 1952; CLARK, 1952) shows that O<sub>2</sub> photo-ionization cannot account for the ionization in region *D*, but can occur at altitudes corresponding to the bottom of the *E*-layer. At the threshold,  $\lambda = 1029$  Å (INN, 1953), the ionization cross-section may be very small (consider the ionization efficiency of O<sub>2</sub>

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obtained by WAINFAN, WALKER, and WEISSLER, 1953). The cross-section at the threshold\* may be as low as  $10^{-19}$  cm<sup>2</sup> (INN, private communication), but the absorption coefficient is probably of the order of  $4 \times 10^{-18}$  cm<sup>2</sup> between 1000 Å and 910 Å. Therefore, an ionization peak of O<sub>2</sub> may occur at 90 km, the height at which the electron concentration could be of the order of  $2 \times 10^4$  cm<sup>-3</sup>. Furthermore, the observation of L- $\alpha$  radiation by rockets down to 74 km (BYRAM, CHUBB, FRIEDMAN, and GAILAR, 1953; BYRAM, CHUBB, and FRIEDMAN, 1954) and in the solar spectrum (PIETENPOL, RENSE, WALZ, STACEY, and JACKSON, 1953; TOUSEY, 1954) shows that the monochromatic radiation of chromospheric hydrogen can be a very effective agent for an ionization process below the mesopause level.

BATES (1952) in studying the atmospheric photo-equilibrium of nitrogen oxides, has shown that the formation of nitric oxide, resulting possibly from three body collisions of nitrogen and oxygen atoms, is counterbalanced by a loss due to a photo-dissociation process, and a chemical reaction between NO and N.

Some time ago it was believed that the absorption band centred at 2264 Å in the solar spectrum observed by DURAND, OBERLY, and TOUSEY (1949) could be identified as a band of *atmospheric* nitric oxide. With this interpretation, the band must correspond to a column of about  $10^{18}$  molecules cm<sup>-2</sup> at about 55 km (BATES and SEATON, 1950). Since MIGEOTTE and NEVEN (1952) have not detected atmospheric nitric oxide in their observations of the solar infrared spectrum, they deduce, by comparison with laboratory measurements, that the total number of nitric oxide molecules is less than  $5 \times 10^{17}$  molecules cm<sup>-2</sup>. More recently, it has been shown (JOHNSON, PURCELL, TOUSEY, and WILSON, 1954) that the absorption observed in rocket spectra, which depresses the solar spectrum, cannot be due to nitric oxide and, therefore, the infrared investigation leads to a possible upper limit for the atmospheric nitric oxide abundance. It can be concluded that the observed absorption is due to solar absorption as yet unidentified.

Possible atmospheric spectroscopic evidence was suggested by NICOLET (1948) when he drew attention to coincidences between  $\beta$ -bands of NO and auroral radiations. The coincidences were found again by VEGARD in subsequent publications, but according to PETRIE and SMALL (1952) NO should not be present in auroral spectra.

Nitrous oxide, however, is observed by infrared spectroscopy. Following discovery of the fundamental band of N<sub>2</sub>O at 7.8  $\mu$  by ADEL (1939), other bands have been found by various workers (MIGEOTTE, 1949); SHAW, SUTHERLAND, and WORMELL, 1948, . . .). From measurements of the absorption of infrared lines, McMATH and GOLDBERG (1949) and MIGEOTTE, BENESCH, and NEVEN (1953) have found a spectroscopically determined abundance of the order of  $10^{19}$  molecules cm<sup>-2</sup>. N<sub>2</sub>O follows the atmospheric vertical distribution (GOLDBERG and MULLER, 1953), or at least may be taken to be a tropospheric constituent. The photochemistry of tropospheric nitrous oxide has been investigated by BATES and WITHERSPOON (1952), who indicate that this molecule is not a member of the main photochemical series of nitrogen oxides. More recently, HARTECK and DONDER (1954) have also considered this problem without any reference to preceding work.

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\* This was written before we had received from Dr. G. L. WEISSLER a manuscript by Dr. P. LEE on the photo-ionization cross-section of O<sub>2</sub>. At 1030 Å the cross-section is  $5 \times 10^{-19}$  cm<sup>2</sup>, indicating that the absorption coefficient of O<sub>2</sub> is very small.

Nitrogen peroxide cannot be considered an important constituent in the mesosphere during daylight, because the dissociation rate coefficient is high. However, the laboratory results show many interesting processes, and  $\text{NO}_2$  formation during the night remains to be investigated. From spectroscopic studies (NORRISH, 1929; BAXTER, 1930) it has been found that *visible* phenomena occur particularly in two bands lying in the red-orange and yellow-green parts of the spectrum; namely, between 6200–6300 Å and 5600–6050 Å. Furthermore, the formation of  $\text{NO}_2$  by a radiative process involving nitric oxide and atomic oxygen is also a process leading to a continuous emission spectrum (GAYDON, 1944). Other laboratory investigations (RAYLEIGH, 1910; STODDARD, 1934; NEWMAN, 1935; SPEALMAN and RODEBUSH, 1935; KONDRATJEV, 1936; TANAKA and SHIMAZU, 1948) point to the fact that there is an afterglow which is related to nitrogen peroxide. Just as for every constituent which can affect the air-glow, it is necessary to study the possible equilibrium with ozone and atomic oxygen, and the departure from photo-equilibrium due to an atmospheric mixing.

In principle, the behaviour of nitrogen oxides must depend on the dissociation of molecular nitrogen. The conditions in the mesosphere and thermosphere indicate that the vertical distribution of nitrogen atoms is determined by atmospheric mixing or diffusion, rather than by local equilibrium. The change in the relative populations of nitrogen oxides must be studied by considering to what extent departure from equilibrium can exist.

After delineating the rate of absorption of solar radiation, the subsequent discussion shows the possible effects produced by atmospheric motions. This analysis will also indicate the rate with which chemical equilibrium is approached and, finally, the effects produced by processes involving nitrogen oxides and leading to possible day and night air-glow.

## II. DISSOCIATION OF NITROGEN MOLECULES

The dissociation of nitrogen molecules has been studied by BATES (1952), who considered the predissociation found by HERZBERG and HERZBERG (1948) in the bands of the Lyman-Birge-Hopfield system. His determination of the dissociation-rate coefficient yields a value  $J_{\text{N}_2} = 10^{-12} \text{ sec}^{-1}$  at zero optical depth. Taking this value, MITRA (1954) has calculated the effect of the optical depth, using a cross-section of  $10^{-19} \text{ cm}^2$  and, therefore, found a rate coefficient decreasing rapidly downward with height in the mesosphere.

Another process is operative in the ionosphere (BATES, 1954). Molecular nitrogen is ionized by ultraviolet radiation of  $\lambda < 796 \text{ Å}$ , and at shorter wavelengths  $\lambda < 661 \text{ Å}$ , for which the absorption coefficient is of the order of  $2 \times 10^{-17} \text{ cm}^2$  (WEISSLER, LEE, and MOHR, 1952). As the number of photons available at the top of the earth's atmosphere is not less than  $2 \times 10^9 \text{ photons cm}^{-2} \text{ sec}^{-1}$  (NICOLET, 1952), the ionization-rate coefficient at zero optical depth (in region *F* at 160–170 km for an overhead sun) cannot be less than  $4.4 \times 10^{-8} \text{ sec}^{-1}$ .

Furthermore, X-ray action is a possible mechanism (NICOLET, 1952a), for the absorption of solar radiation from 175 Å to the shortest wavelengths can be effective for ionization. According to rocket results (BURNIGHT, 1952; TOUSEY, 1952; BYRAM, CHUBB, and FRIEDMAN, 1953), X-rays near 7 Å were detected above 90 km.

More recently, BYRAM, CHUBB, and FRIEDMAN (1954, private communication) have obtained new values. According to their latest two results, the number of photons  $\text{cm}^{-2} \text{sec}^{-1}$  is equal to  $2 \times 10^7$  or  $10^9$  for the spectral range  $20 \text{ \AA}$  to  $8 \text{ \AA}$ , and  $3 \times 10^8$  or  $3 \times 10^9$  for wavelengths shorter than  $60 \text{ \AA}$ .

From these two sets of values, which are, however, widely divergent, it can be stated that, if the scale height is of the order of 10 km, the rate of direct ionization at the peak for  $\lambda < 60 \text{ \AA}$  must be between 1000 and 100 electrons  $\text{cm}^{-3} \text{sec}^{-1}$ . Since about 70 per cent of the electron production with  $\lambda < 60 \text{ \AA}$  arises from  $\text{N}_2$ , only 30 per cent must be associated with the *E*-layer formation.\* It must be pointed out that the solar X-ray emission is not limited to wavelengths shorter than  $60 \text{ \AA}$ . So far as the ionization of nitrogen molecules is concerned, we can state that at least 100  $\text{N}_2$  molecules are ionized per sec and  $\text{cm}^3$  in region *E*. Therefore, about 1000 nitrogen atoms can be produced per sec and  $\text{cm}^3$  at such low heights as 110 km. In fact, ionization of molecular nitrogen is followed by dissociative recombination (BATES and MASSEY, 1947) after a very short time. The lifetime  $\tau_{\text{N}_2^+}$  of a nitrogen ion is

$$\tau_{\text{N}_2^+} = 1/\alpha n_e,$$

and depends on the electron concentration  $n_e$  in the ionosphere. The dissociative recombination coefficient of  $\text{N}_2^+$  is not less than  $10^{-7} \text{ cm}^3 \text{sec}^{-1}$  (BIONDI, 1951; FAIRE, FUNDINGSLAND, and ADEN, 1954), and as low an electron concentration as  $10^4 \text{ cm}^{-3}$  results in a lifetime of  $\text{N}_2^+$  of less than one hour. Thus, in the whole ionosphere, the photo-ionization by ultraviolet radiation and X-rays leads to a yield of nitrogen atoms which is larger than the production by the primary dissociation process.

The results, however, concern only a static atmosphere in which no transport process is involved. It was shown by NICOLET and MANGE (1954), and NICOLET (1954), that dynamic processes such as diffusion and mixing are acting on the vertical distribution of molecular oxygen. A similar problem exists for atomic nitrogen after its production. It can be shown that the downward diffusion velocity at 160 km (unit optical depth for an overhead sun) is about  $1 \text{ m sec}^{-1}$ . The yield of nitrogen atoms versus height, therefore, cannot be computed without consideration of atmospheric transport. Downward transport of nitrogen atoms following an ionization process is strongly effective, and modifies the vertical distribution of the nitrogen atom concentration, computed on the basis of a photo-equilibrium in a static atmosphere.

This analysis of  $\text{N}_2$  dissociation is different from those of DEB (1952) and SATO (1953), for these authors do not consider the possibility of ionization by X-rays, and have adopted a radiative recombination of normal nitrogen atoms with a coefficient not less than  $10^{-21} \text{ cm}^3 \text{sec}^{-1}$ . With such a value the lifetime  $\tau_{\text{N}}$  of a nitrogen atom is

$$\tau_{\text{N}} = 1/10^{-21}n(\text{N});$$

\* It must be pointed out that only a fraction of the total electron production by X-ray action (1/5 at wavelengths for which the absorption coefficients for oxygen and nitrogen are of the same order) is associated with the ionospheric layers as observed by radio methods. The excess observed in the X-ray spectrum by BYRAM, CHUBB, and FRIEDMAN (1954) does not necessarily mean a high ratio of negative ions to electrons in the *E*-layer, but can be interpreted by means of rapid dissociative recombination of  $\text{N}_2^+$  compared with that of  $\text{O}_2^+$ .

that is to say, a very long time. In fact, the loss of nitrogen atoms primarily depends on the association of nitrogen and oxygen atoms in a three-body collision, and the shortest lifetime is

$$\tau_N = 1/10^{-32}n(M) n(O)$$

in which  $n(M)$  denotes the third-body concentration. In order to have a lifetime shorter than one year, it is necessary that the concentrations  $n(M)$  and  $n(O)$  be larger than  $10^{12} \text{ cm}^{-3}$ . Therefore, ionization of molecular nitrogen followed by dissociative recombination and vertical transport due to diffusion and mixing is a powerful process for the production of atomic nitrogen in the lower thermosphere. Furthermore, the vertical distribution of nitrogen atoms does not depend on a dissociation equilibrium state, but on atmospheric motions affecting a static equilibrium.

### III. THE VERTICAL DISTRIBUTION OF NITROGEN OXIDES IN THE MESOSPHERE

The formation of nitric oxide is due *a priori* to a three-body collision process



or to nitrous oxide formation and subsequent photo-dissociation



Reaction (1) is certainly the primary process of NO formation; it requires the dissociation of nitrogen as indicated in Section II. Process (2) should lead to NO formation in a region in which the atomic oxygen concentration is maximum; namely, above the mesopause level. However, in their study of the absorption coefficients of nitrous oxide, ZELIKOFF, WATANABE, and INN (1953) and ZELIKOFF and ASCHENBRAND (1954) have interpreted absorption continua in terms of possible dissociation processes without dissociation into nitric oxide and atomic nitrogen. According to this interpretation, process (2) should not be considered as a fundamental mechanism for the production of nitric oxide, and it is, therefore, difficult to believe that the photo-dissociation of  $\text{N}_2\text{O}$  provides a contribution to the production of nitrogen atoms at levels of the order of 80 km, as MITRA (1954) has found. Consequently, reference must be made to the results of BATES and WITHERSPOON in which  $\text{N}_2\text{O}$  is a tropospheric constituent.

Since the loss of nitric oxide molecules is due to photo-dissociation, for which the rate coefficient (BATES, 1952) is of the order of  $10^{-7} \text{ sec}^{-1}$ , and to the reaction (BATES, 1952)



the time of dissociation,  $\tau_{\text{dis}}(\text{NO})$ , of nitric oxide may be very long. Consequently, it is unrealistic to deduce its concentration from photo-equilibrium conditions. Furthermore, a reaction such as



is to be considered, and may be important at night.

## A study of nitrogen peroxide formation and photo-dissociation



shows that the ratio  $n(\text{NO}_2)/n(\text{NO}) \ll 1$ , and there is no practical effect on the daytime nitric oxide concentration.

It is clear, therefore, that atmospheric mixing, acting during the day, can play a leading role in fixing the vertical distribution of NO. Nitric oxide can follow the variation of the atmospheric distribution in the mesosphere more closely than a vertical distribution determined by photo-equilibrium conditions.

We make one further comment about the influence of  $\text{NO}_2$ . As will be shown later, the ratio  $n(\text{NO}_2)/n(\text{NO})$  varies very rapidly, and is different during day and night. However, so far as the region *D* problem is concerned, the photo-dissociation-rate coefficient of nitrogen peroxide must be considered. Because its value is about  $5 \times 10^{-3} \text{ sec}^{-1}$  (BATES, 1952), the lifetime of an  $\text{NO}_2$  molecule is very short, 200 seconds, and a daytime photo-equilibrium exists for this molecule. But, since the ratio  $n(\text{NO}_2)/n(\text{NO})$  remains less than unity, the other vertical distributions are not affected.

## IV. THE TOTAL NUMBER OF NITRIC OXIDE MOLECULES

Since it is obvious that there is no possibility of avoiding a departure from photo-chemical equilibrium for nitric oxide in the mesosphere, the formation of a *D*-layer is to be found, to a first approximation, with NO molecules following the atmospheric vertical distribution.

No direct experimental data are available concerning this, and one must conjecture concerning possible numerical values. Dissociative recombination of  $\text{NO}^+$  is certainly an important process, but it is not possible to determine which value of the recombination coefficient is the most probable in the range  $10^{-6} \text{ cm}^3 \text{ sec}^{-1}$  to  $10^{-8} \text{ cm}^3 \text{ sec}^{-1}$ . On the other hand, it is not easy to obtain a correct value from ionospheric data, as may be seen from the values collected by MITRA and JONES (1954). These authors obtain a smooth curve leading to a recombination coefficient varying continuously with height. However, the actual heights cannot be well determined. If, for example,  $10^{-7} \text{ cm}^3 \text{ sec}^{-1}$  is adopted as the value of the recombination coefficient, it may be in error by one order of magnitude, and it may be concluded that any deductions from an ionization equilibrium equation will be subject to considerable uncertainty. Nevertheless, it is possible to find permissible limits for the nitric oxide concentration.

MIGEOTTE and NEVEN (1952) have determined an upper limit for  $n(\text{NO})H$  of  $< 5 \times 10^{17} \text{ cm}^{-2}$ ; hence,  $H$  being the scale height, any concentration  $n(\text{NO}) > 10^{12} \text{ cm}^{-3}$ , found by theory, cannot be acceptable. If a layer of 10 km thickness exists with more than  $5 \times 10^{11} \text{ NO molecules cm}^{-3}$ , nitric oxide would have been detected by infrared methods. Thus, it is safe to conclude that a NO concentration larger than  $10^{11} \text{ cm}^{-3}$  does not exist in the mesosphere, and the large concentrations found by MITRA (1954) are not acceptable. This conclusion is confirmed from the interpretation of rocket data.

Because NO has an absorption coefficient of the order of  $2 \times 10^{-18} \text{ cm}^2$  (SUN

and WEISSLER, 1952; WATANABE, MARMO, and INN, 1953) a unit optical depth is found for  $5 \times 10^{17}$  molecules  $\text{cm}^{-2}$ , or less than  $10^{12}$  molecules  $\text{cm}^{-3}$ . Since solar Lyman- $\alpha$  is observed down to  $74 \pm 2$  km for a solar elevation of  $18\text{--}20^\circ$  (BYRAM, CHUBB, FRIEDMAN, and LICHTMAN, 1952), NO does not absorb  $L\alpha$  more than  $\text{O}_2$ . At about 80 km, the unit optical depth at  $L\alpha$  for an overhead sun can occur only if  $\text{O}_2$  molecules are the effective absorbing constituent. The transmission factor would be about 10 per cent near 72.5 km and 1 per cent near 67.5 km, when  $\text{O}_2$  absorbs alone and the sun is overhead. With an  $18\text{--}20^\circ$  solar elevation, a 1 per cent transmission factor would correspond to about 75 km. Hence, it is not possible to include NO as an atmospheric constituent strongly affecting the optical depth for  $L\alpha$ , because the solar radiation could not arrive at so low a height as 75 km. The ratio  $n(\text{NO})/n(\text{M})$ , namely the ratio of nitric oxide to all the atmospheric constituent concentrations, is less than 1/1000. A more recent analysis by BYRAM, CHUBB, FRIEDMAN, and GAILAR (1953) shows that no influence of nitric oxide can be detected. Since the absorption cross-section for NO is  $2.4 \times 10^{-18}$   $\text{cm}^2$ , with an ionization cross-section equal to  $2.1 \times 10^{-18}$   $\text{cm}^2$  (WATANABE, 1954), and since the absorption cross-section of  $\text{O}_2$  is of the order of  $10^{-20}$   $\text{cm}^2$  (PRESTON, 1940; WATANABE, INN, and ZELIKOFF, 1953; DITCHEBURN, 1954), a ratio  $n(\text{NO})/n(\text{M}) = 1/1000$  should give an almost identical absorption for NO and  $\text{O}_2$ . Therefore, the concentration of nitric oxide cannot be more than  $10^{11}$   $\text{cm}^{-3}$  at 80 km. Consequently, rocket data and infrared spectroscopy yield consistent results indicating that there are, at any height, less than  $10^{11}$  NO molecules  $\text{cm}^{-3}$ .

#### V. THE PHOTO-IONIZATION OF NITRIC OXIDE AND ITS CONCENTRATION

The rate of electron production by photo-ionization of NO may be written as follows.

$$n(\text{NO})K(\text{NO})Q_\infty(L\alpha)e^{-n(\text{O}_2)K(\text{O}_2)H \sec \chi}, \quad (7)$$

in which  $K(\text{NO})$  denotes the ionization cross-section of NO, and  $K(\text{O}_2)$  the absorption coefficient of molecular oxygen. The absorption cross-section of NO must not be considered in the optical depth.

The vertical distribution of the number of photons available for the photo-ionization of NO depends on the molecular oxygen concentration at efficient optical depths; the peak of the electron production by NO lies practically at the  $\text{O}_2$  absorption peak for  $L\alpha$  radiation. If the nitric oxide concentration does not behave very differently from the concentrations of the principal atmospheric constituents, the peak of photo-ionization is fixed by the condition, (7),

$$n(\text{O}_2)K(\text{O}_2)H \sec \chi = 1 + \beta, \quad (8)$$

where  $\beta = dH/dz$  is the gradient of the atmospheric scale height,  $H$ .

If the nitric oxide distribution is different from the atmospheric distribution, but related to it through the parameter  $X$  according to

$$[n(\text{NO})/n_0(\text{NO})]^X = n(\text{O}_2)/n_0(\text{O}_2),$$

the peak of photo-ionization is determined by

$$n(\text{O}_2)K(\text{O}_2)H \sec \chi = X(1 + \beta). \quad (8')$$

Thus, the actual problem of NO ionization is not so complex as when a photo-equilibrium of nitrogen oxides is to be considered. The number of photons available for the ionization is known, the atmospheric absorption of  $L\alpha$  can be determined, and the vertical distribution of NO is not unknown. Consequently, it should be possible to determine the concentration of NO. Condition (8) shows a peak, for an overhead sun, of between 75 and 77 km, where the total number of atmospheric molecules is of the order of  $7 \times 10^{20} \text{ cm}^{-2}$  or  $5 \times 10^{20} \text{ cm}^{-2}$ .

The number of photons available at zero optical depth for a quiet sun has been obtained by BYRAM, CHUBB, FRIEDMAN, and GAILAR (1953). It is of the order of  $6 \times 10^9 \text{ photons sec}^{-1} \text{ cm}^{-2}$ . At the absorption peak the number available must be of the order of  $2.2 \times 10^9 \text{ photons sec}^{-1} \text{ cm}^{-2}$ . Since the ionization cross-section of NO is  $(2.1 \pm 0.2) \times 10^{-18} \text{ cm}^2$  (WATANABE, 1954), the ionization rate coefficient equals  $4.5 \times 10^{-9} \text{ sec}^{-1}$  at the absorption peak, and  $1.3 \times 10^{-8} \text{ sec}^{-1}$  at zero optical depth for a quiet sun. These values may be compared with those considered by MITRA (1954). Introduction of his reduction factor, namely  $2.6 \times 10^{-3}$  or  $1.6 \times 10^{-1}$ , cannot be accepted, and shows that the concentrations deduced from his equations are not correct.

Using the conventional equation for an ionization equilibrium, that is,

$$\frac{n^+(\text{NO})n_e}{n(\text{NO})} = \frac{4.5 \times 10^{-9}}{\alpha} e^{-n(\text{O}_2)K(\text{O}_2)H \sec \chi}, \quad (9)$$

in which  $n^+(\text{NO})$  denotes the number of positive ions,  $n_e$  the electron concentration, and  $\alpha$  the ionospheric recombination coefficient, it is clear that the concentration of NO could be deduced if the ionospheric parameters such as electron concentration and recombination were well known. It is difficult to say what value of  $n_e$  between  $10^3$  and  $10^4 \text{ cm}^{-3}$  is acceptable for the largest concentration in region *D*, and what value of  $\alpha$  can be chosen.

Arbitrarily taking  $10^8/\text{NO}$  molecules  $\text{cm}^{-3}$  at 80 km, that is to say a concentration of  $2 \times 10^{-7}$  times the atmospheric concentration, the rates of ionization for an overhead sun would be:

km	85	80	75	70	65
$n_e \text{ cm}^{-3} \text{ sec}^{-1}$	0.58	0.77	0.78	0.30	0.025

A recombination coefficient equal to  $10^{-6} \text{ cm}^3 \text{ sec}^{-1}$  would give an electron concentration of  $1000 \text{ cm}^{-3}$  at 77 km.\* However, the effect of negative ions should be taken into account at the lowest heights. Therefore, the peak value of the electronic concentration depends on the assumed values of the parameters.†

Since neutral sodium has a concentration peak above 80 km (HUNTEN, 1954) of the order of  $10^4 \text{ cm}^{-3}$ , the number of electrons produced by ionization of this atmospheric constituent at 85 km is not more than  $10^4 \times 10^{-5} = 10^{-1} \text{ cm}^{-3} \text{ sec}^{-1}$ ;

\* For example,  $\alpha = 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$ , and  $n(\text{NO}) = 5 \times 10^8 \text{ cm}^{-3}$  at 80 km, lead to about  $6 \times 10^3$  electrons  $\text{cm}^{-3}$  at the peak.

† A photo-detachment rate coefficient of  $0.5 \text{ sec}^{-1}$ , and an attachment coefficient of the order of  $10^{-18} \text{ cm}^3 \text{ sec}^{-1}$ , lead to a value of  $\lambda = n^-/n_e$  of the order of unity at 68 km. But, at 80 km,  $\lambda$  would be only 0.2, and therefore, the electron concentration peak cannot be more than one scale height above the electron production peak. In other words, if the dissociative recombination coefficient were  $10^{-6} \text{ cm}^3 \text{ sec}^{-1}$ , the ionospheric coefficient would be  $4 \times 10^{-6}$  at 60 km,  $2.5 \times 10^{-6}$  at 65 km, about  $2 \times 10^{-6}$  at 70 km, and  $1.2 \times 10^{-6}$  at 80 km.

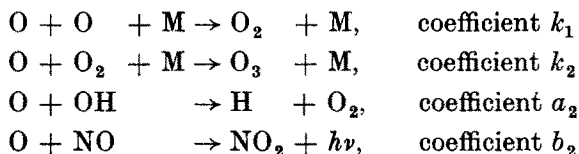


a maximum value. This demonstrates how important it is to obtain exact ionospheric data on recombination coefficients and of electronic concentration versus exact height. In conclusion, if a nitric oxide concentration of  $10^8 \text{ cm}^{-3}$  is considered correct to within one order of magnitude, it leads to a possible explanation of the behaviour of region *D* under normal conditions as well as under solar flare conditions. Sodium atoms cannot be responsible for the ionization at the bottom of the region, for their concentration appears to decrease too rapidly below their peak at 85 km. Insofar as the upper part of region *D* is concerned, at altitudes of 90 km, it will be necessary to take into account the variation of the ionospheric recombination coefficient with height, or the penetration of solar radiation ionizing  $\text{O}_2$  near its threshold at about 1030 Å, for here the absorption coefficient is less than  $10^{-18} \text{ cm}^2$  and permits the penetration of solar radiation below 100 km.

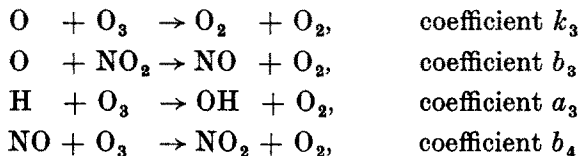
## VI. PROCESSES IN THE CHEMOSPHERE

In the chemosphere, the aeronomic problem depends on the recombination processes leading to a loss of oxygen atoms. In a pure oxygen atmosphere, the loss of oxygen atoms is due to ozone formation, and association of atoms into oxygen molecules. It was shown by BATES and NICOLET (1950) that by its catalytic action hydrogen may have an effect on the ozone concentration in the mesosphere. Furthermore, dynamic motions which tend to increase the atomic oxygen concentration downward (NICOLET and MANGE, 1954; NICOLET, 1954) modify the photo-equilibrium picture when the times involved in the reactions are too long. These motions are particularly effective near the mesopause level.

At night, atomic oxygen can enter into various reactions leading, finally, to a molecular recombination as follows:



Subsequently, the following reactions are also possible leading to  $\text{O}_2$ :



An approximate equilibrium equation may be obtained at a height of the order of 70 km, the processes being considered as sufficiently rapid, namely,

$$n(\text{H})/n(\text{OH}) \simeq n(\text{O})/n(\text{O}_3).$$

At greater heights, departure from the equilibrium can exist, because the time of recombination of oxygen atoms increases with height (NICOLET and MANGE, 1954). Thus, the processes involving nitrogen oxides are subject to the variation of the atomic oxygen concentration.

In the mesosphere above 50 km, the atomic oxygen concentration is larger than the ozone concentration under *daytime* photo-equilibrium conditions. Therefore, the aeronomic problem is different above or below 50 km. If the mesosphere were a pure oxygen atmosphere, the ozone vertical distribution (BATES and NICOLET, 1950) would be

$$n(\text{O}_3)_{\text{limit}} = \frac{k_2}{k_3} n(\text{O}_2)n(\text{M}).$$

Above 80 km  $n(\text{O}_3)_{\text{limit}} < n(\text{O})_{\text{day}}$ , and the atomic oxygen concentration always remains larger than the ozone concentration. Below 75 km, the ozone concentration cannot be larger than the daytime atomic oxygen concentration.

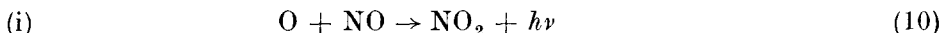
The fundamental process involving ozone and atomic oxygen depends on a reaction with an energy of activation of the order of 6 kcal leading to a rate coefficient,  $k_3$ , of about  $10^{-15} \text{ cm}^3 \text{ sec}^{-1}$  at  $250^\circ\text{K}$ . But the processes affecting atomic oxygen and ozone through the catalytic action of hydrogen require a lower activation energy, perhaps of the order of 3 kcal, leading to a rate coefficient,  $a_2 \approx a_3$ , of more than  $10^{-13} \text{ cm}^3 \text{ sec}^{-1}$  at  $250^\circ\text{K}$ . Thus, as was shown by BATES and NICOLET (1950), the atomic oxygen-ozone equilibrium in the mesosphere is subject to the catalytic action of hydrogen. Nevertheless, these estimates may be in error by a considerable factor, due to lack of precise values for the chemical reactions; it is difficult to study the exact variation of OH, H, O, and  $\text{O}_3$  during dark hours.

The chemical reactions concerning the nitrogen oxides will be processes of the same kind. However, a considerable amount of attention must be given to the possible concentrations before studying the aeronomic problem. In the following, it is possible to suggest a scheme which is not a combination of all possibilities, but based on reactions of high efficiency due to low energies of activation.

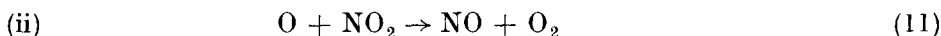
## VII. NITROGEN PEROXIDE

As may be readily verified from Bates's equations (1952) and the rate coefficient values, the photo-ionization of nitrogen peroxide is so rapid during the day that its action on the nitric oxide concentration can be neglected in the upper mesosphere.

The essential night-time mechanisms affecting  $\text{NO}_2$  are:



for which the rate coefficient  $b_2$  is about  $10^{-17} \text{ cm}^3 \text{ sec}^{-1}$  (BATES, 1954).



for which the rate coefficient  $b_3$  depends on the activation energy chosen. Data may be deduced from SCHUMACHER (1930), SPEALMAN and RODEBUSH (1935), and HENRIQUES, DUNCAN, and NOYES (1938). The probability of this reaction is of the order of  $10^{-5}$  per collision at a temperature of  $313^\circ\text{K}$ . Without any steric factor the activation would be 7 kcal, and with a steric factor of 0.01, as indicated by HENRIQUES, DUNCAN, and NOYES (1938), the activation energy may be 4.3 kcal. However, a steric factor of the order of  $10^{-3}$  cannot be excluded after one considers other reactions of the same type. With such a value, the activation energy would

be only 2.9 kcal. Adopting as extreme values 7 kcal and 2.9 kcal, the following values are obtained:

$T(^{\circ}\text{K})$	$E = 7 \text{ kcal}$	$E = 4.2 \text{ kcal}$	$E = 2.9 \text{ kcal}$
150	$1.2 \times 10^{-20}$	$7.0 \times 10^{-18}$	$1.1 \times 10^{-17}$
200	$4.8 \times 10^{-18}$	$5.2 \times 10^{-17}$	$1.4 \times 10^{-16}$
250	$1.8 \times 10^{-16}$	$4.9 \times 10^{-16}$	$6.9 \times 10^{-16}$
300	$2.1 \times 10^{-15}$	$2.3 \times 10^{-15}$	$2.0 \times 10^{-15}$
350	$1.2 \times 10^{-14}$	$6.8 \times 10^{-15}$	$4.3 \times 10^{-15}$

If a value of  $2 \times 10^{-15} \text{ cm}^3 \text{ sec}^{-1}$  is accepted at  $300^{\circ}\text{K}$ , a minimum value of  $5 \times 10^{-18} \text{ cm}^3 \text{ sec}^{-1}$  and a maximum value of  $1 \times 10^{-16} \text{ cm}^3 \text{ sec}^{-1}$  must be adopted at  $200^{\circ}\text{K}$ . Because the experimental value given by SPEALMAN and RODEBUSH (1935) is an estimate correct only to an order of magnitude ( $10^{-5}$  per collision at  $40^{\circ}\text{C}$ ), it is difficult to determine an exact value at temperatures of the upper mesosphere.



The rate coefficient for (iii),  $b_4$ , has been determined (JOHNSTON and CROSBY, 1951, 1954).

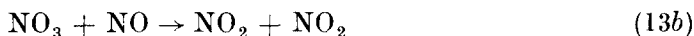
Taking a steric factor of  $5 \times 10^{-3}$  and an activation energy of 2.4 kcal, the following values are obtained for  $b_4$ :

$$\begin{array}{ll} 150^{\circ}\text{K}, 3 \times 10^{-16}; & 200^{\circ}\text{K}, 2.5 \times 10^{-15} \\ 250^{\circ}\text{K}, 9.5 \times 10^{-15}; & 300^{\circ}\text{K}, 2.3 \times 10^{-14} \end{array}$$

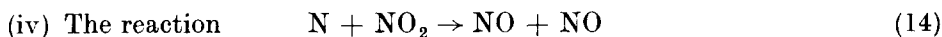
Of the reactions



followed by



(13a) has been studied in the laboratory by JOHNSTON and YOST (1949) and can be neglected to a first approximation, since its activation energy of about 7 kcal with a steric factor of the order of  $4 \times 10^{-2}$  leads to a rate coefficient of less than  $10^{-17}$  at  $250^{\circ}\text{K}$ . For this reason, (13b), which has no activation energy (JOHNSTON, 1951), may be neglected.



is a fairly rapid reaction studied by SPEALMAN and RODEBUSH (1935). According to their conclusion, the reaction (14) and



are of the same order of rapidity at  $40^{\circ}\text{C}$  as that (11) between nitrogen peroxide and oxygen atoms. It should be of extreme importance to know the steric factors and activation energies associated with  $b_5$  and  $b_6$ , the rate coefficients of (14) and (3), respectively.

VETTER (1949) has obtained values for the steric factors and activation energies of (3), (11), and (14). However, the whole study of VETTER depends on a reaction

$O + NO \rightarrow O_2 + N$ , which is endothermic to the extent of 32 kcal. Therefore, the activation energy deduced by VETTER is 29 kcal; that is to say, a smaller value than that needed by the endothermic reaction. Data presented by WISE and FRECH (1952) lead to an activation energy of about 23 kcal. These various results cannot be accepted, since the equilibrium constant  $K(N_2)$  of the reaction  $N_2 = 2N$  is based on heats of dissociation of the order of 170 kcal instead of 225 kcal.

Consequently, the lack of exact data necessitates very crude estimates. Because an almost linear collision is involved in such reactions, we consider that a steric factor of  $10^{-2}$  should be a maximum value, and that a value of  $10^{-3}$ , which will be a minimum, cannot be far from the real steric hindrance. Such a value leads to the adoption of an activation energy of about 2.9 kcal. A steric factor of  $5 \times 10^{-3}$ , like that for (12), would lead to an activation energy of about 4 kcal.



is a reaction for which the dissociation rate coefficient  $J_{NO_2}$  is  $5 \times 10^{-3} \text{ sec}^{-1}$  (BATES, 1954), when  $NO_2$  is subject to solar radiation.

Neglecting possible reactions with hydrogen, the differential equation involving processes affecting  $NO_2$  may be the following:

$$\frac{dn(NO_2)}{dt} = [b_2n(O) + b_4n(NO)n(O_3)]n(NO) - [b_3n(O) + b_5n(N) + J_{NO_2}]n(NO_2). \quad (16)$$

During the day, the time of dissociation,  $\tau_{\text{diss}}(NO_2)$ , of nitrogen peroxide will be given by

$$\tau_{\text{diss}}(NO_2) = 1/J_{NO_2} = 200 \text{ sec} \quad (17)$$

which is a very short time. A photo-equilibrium must, therefore, exist and the equation is

$$\frac{n(NO_2)}{n(NO)} = \frac{b_2n(O) + b_4n(O_3)}{J_{NO_2} + b_3n(O) + b_5n(N)}. \quad (18)$$

Inserting numerical values in (18), we see that  $n(NO_2)$  is only a fraction of  $n(NO)$ , for  $T = 250^\circ\text{K}$ ,

$$\frac{n(NO_2)}{n(NO)} = 2 \times 10^{-15}n(O) \quad (19)$$

or

$$\frac{n(NO_2)}{n(NO)} = 2 \times 10^{-12}n(O_3). \quad (20)$$

After twilight, the ratio  $n(NO_2)/n(NO)$  increases according to the solution to the differential equation (16) in which  $J_{NO_2} = 0$ , and  $b_3n(O) > b_5n(N)$ ,

$$n(NO_2) = n_0(NO_2)e^{-b_3n(O)t} + \frac{b_2n(O) + b_4n(O_3)}{b_3n(O)} n(NO) [1 - e^{-b_3n(O)t}] \quad (21)$$

provided  $n(NO)$  and  $n(O)$  do not vary appreciably.

At sunset, the concentration of nitrogen peroxide increases according to the rate equation

$$\frac{dn(\text{NO}_2)}{dt} = [b_2n(\text{O}) + b_4n(\text{O}_3)] n(\text{NO}). \quad (22)$$

Above the mesopause  $b_2n(\text{O}) > b_4n(\text{O}_3)$  and (22) becomes

$$\frac{dn(\text{NO}_2)}{dt} = 10^{-17} n(\text{O}) \quad (23)$$

which gives, after only  $10^3$  seconds,

$$n(\text{NO}_2) \geq n(\text{NO})/100 \quad (24)$$

if

$$n(\text{O}) \geq 10^{12} \text{ cm}^{-3}.$$

In the mesosphere at  $T = 250^\circ\text{K}$  where  $n(\text{O}_3) > n(\text{O})/1000$ , (22) becomes

$$\frac{dn(\text{NO}_2)}{dt} = 10^{-14} n(\text{O}_3) n(\text{NO}) \quad (25)$$

which yields, after  $10^3$  seconds, if  $n(\text{O}_3)$  is of the order of  $10^{10} \text{ cm}^{-3}$ ,

$$n(\text{NO}_2) = n(\text{NO})/10. \quad (26)$$

In fact, the time  $\tau_{\text{neq}}$  to reach the nocturnal equilibrium value,

$$\frac{n(\text{NO}_2)}{n(\text{NO})} = \frac{b_2n(\text{O}) + b_4n(\text{O}_3)}{b_3n(\text{O})}, \quad (27)$$

which is expressed by

$$\tau_{\text{neq}} = 1/b_3n(\text{O}), \quad (28)$$

depends on the atomic oxygen concentration and varies with height. Adopting the daytime value of  $n(\text{O})$ , the time of  $\text{NO}_2$  formation defined by (28) should be of the order of  $10^4$  to  $5 \times 10^4$  sec between 50 km and 90 km. In other words, one night may be necessary to reach equilibrium instead of the 200 sec for a sunlit atmosphere. If we consider daytime values, the ratio  $n(\text{NO}_2)/n(\text{NO})$  is less than unity above 50 km, while it is larger than unity below 50 km where the temperature is still sufficiently high.

During dark hours, the equilibrium ratio  $n(\text{NO}_2)/n(\text{NO}) > 1$  in the whole region where ozone is efficient. At 90 km, for example, where the reaction involves oxygen atoms, the equilibrium value cannot reach unity.

Day and night conditions may become identical in the thermosphere. For example, with the values adopted,  $n(\text{NO}_2)/n(\text{NO})$  should be of the order of  $3 \times 10^{-3}$  during night and day at 120 km.

Although it is necessary to avoid conclusions based only on night-time equilibrium conditions, it may still be remarked that, during the dark hours, the transformation of  $\text{NO}$  into  $\text{NO}_2$  is important throughout the entire mesosphere. At lower heights, ozone molecules play the leading role, while above mesopause levels the reaction is due, essentially, to oxygen atoms.

It is important to point out that ozone would be destroyed during dark hours in the mesosphere if the nitric oxide concentration were larger than the ozone concentration. If not, the loss of ozone molecules is given by

$$\frac{dn(\text{O}_3)}{dt} = -b_4 n(\text{O}_3) n(\text{NO}). \quad (29)$$

Therefore,

$$n(\text{O}_3) = n_0(\text{O}_3) e^{-b_4 n(\text{NO})t} \quad (30)$$

would lead to about one-third of the initial concentration,  $n_0(\text{O}_3)$ , in less than 2000 sec at 50 km, where the temperature is 280°K and  $n_0(\text{O}_3) = 3 \times 10^{10} \text{ cm}^{-3}$ ; consequently,  $n(\text{NO})$  should be less than  $n_0(\text{O}_3)$ . It seems that the nitric oxide concentration should be less than the ozone concentration below 70 km ( $n(\text{NO}) \leq 10^9 \text{ cm}^{-3}$ ) to avoid an ozone loss during the night. Furthermore, the nocturnal concentration of nitrogen peroxide is limited to that of the daytime nitric oxide in the entire mesosphere.

Using the complete set of reactions written above, the equation governing the rate of change of  $n(\text{NO})$  is

$$\begin{aligned} \frac{dn(\text{NO})}{dt} = & b_1 n(\text{M}) n(\text{O}) n(\text{N}) + [J_{\text{NO}_2} + b_3 n(\text{O}) + 2b_5 n(\text{N})] n(\text{NO}_2) \\ & - [J_{\text{NO}} + b_2 n(\text{O}) + b_4 n(\text{O}_3) + b_6 n(\text{N})] n(\text{NO}). \end{aligned} \quad (31)$$

Using (18), (31) can be written

$$\frac{dn(\text{NO})}{dt} = b_1 n(\text{M}) n(\text{O}) n(\text{N}) - [J_{\text{NO}} + b_6 n(\text{N})] n(\text{NO}),$$

for

$$b_3 n(\text{O}) > b_5 n(\text{N}). \quad (32)$$

One can say from (32), written for photo-equilibrium conditions, that the ratio  $n(\text{NO})/n(\text{N})$  would decrease from about 50 at 50 km to about unity at 90 km. Maximum equilibrium values corresponding to night-time conditions would lead to NO concentrations of about  $5 \times 10^9 \text{ cm}^{-3}$ .

These results are only estimates which suffer from lack of precision of experimental data. Furthermore, since an equilibrium cannot be reached, departures from photo-equilibrium conditions occur throughout the whole mesosphere and in the thermosphere. The mixing effect will be prevalent in the mesosphere and lower thermosphere, while diffusion will play the leading role above the production peak of nitrogen atoms.

In any case, it is important to distinguish between day and night conditions which affect the equilibrium between NO and NO<sub>2</sub> in the mesosphere, particularly in the region where the night-time equilibrium ratio  $n(\text{NO}_2)/n(\text{NO})$  is larger than unity.

Before studying the exact variation of the NO<sub>2</sub> nocturnal concentration, it is necessary to study the complete problem involving ozone, OH, H, and other processes, in a nitrogen-oxygen atmosphere in which departures from equilibrium conditions do exist.

## VIII. CONCLUSIONS

Following BATES's analysis of the photochemistry of nitrogen oxides, it is possible to develop the study of the aeronomic problem of nitric oxide and nitrogen peroxide.

First, it is necessary to consider the dissociation of molecular nitrogen due to the photo-ionization of  $N_2$  by ultraviolet radiation in region *F* with a departure from photochemical equilibrium conditions. Second, the photo-ionization of  $N_2$  by X-rays in region *E* leads to a peak production of about 1000 nitrogen atoms per  $cm^3$  and sec. Since the mean lifetime of a nitrogen atom before molecular formation is  $1/b_1n(M)n(O)$ , it is shorter in the *E*-layer than in region *F*, and departures from photochemical equilibrium are less severe than at higher levels. Nevertheless mixing effects do play a role, and lead to fluctuations in the nitric oxide production below 100 km. These may give increases in the electron density in region *D* even when the sun is quiet. In other words, variations in the ionization of the *D*-layer may occur as a result of atmospheric motions affecting the downward transport of NO.

It was shown by NICOLET (1954) that concentrations of atomic oxygen which are larger than those given by photochemical equilibrium do exist in the  $O_2$ -O transition region because of atmospheric motions. The same kind of problem exists for nitric oxide. Therefore a special study should be made near 100 km.

In considering the problem of the origin of region *D*, the nitric oxide concentration may be taken to be about 5 to  $1 \times 10^8 cm^{-3}$  near 80 km, and would be of the order of 5 to  $1 \times 10^9 cm^{-3}$  at 65 km, generally corresponding to a vertical distribution following the atmospheric distribution, or even decreasing more slowly than the atmospheric constituents.

Such concentrations are able to provide an interpretation of the *D*-layer, subject to the effect of  $L\alpha$  emitted by a quiet sun, and also to the effect of solar flares. Furthermore, fluctuations occurring in nitric oxide concentrations and subject to atmospheric motions may modify the ionization rate without any variation in  $L\alpha$ . Unfortunately, exact values of the ionospheric parameters cannot be used, for the altitudes deduced from ionospheric measurements are not precise enough, nor are the electron concentrations well known.

Between 90 km and 100 km ionospheric behaviour is difficult to determine without any knowledge of the X-ray radiation between 40 Å and 30 Å. Now, considering the ionization produced by ultraviolet radiation, it is easy to show (NICOLET, 1952) that the solar radiation at 1030 Å depends on free-free coronal transitions. Adopting coronal temperatures between 740,000°K and 1,440,000°K, numerical results can be obtained, using NICOLET's formulae (1952). The number of photons  $sec^{-1} cm^{-2}$  at the top of the earth's atmosphere between 1040 and 920 Å, i.e., in the spectral range not subject to a continuous absorption by atomic oxygen and molecular nitrogen, would be  $10^7$  to  $5 \times 10^7$ . Therefore, the solar emission cannot be represented by radiation temperatures less than 4500°K at about 1040 Å.

The aeronomic process of  $O_2$  ionization depends on the continuous absorption of  $O_2$  at its first ionization potential. At the threshold, the ionization cross-section is small (as low as  $5 \times 10^{-19} cm^2$ ). However, the absorption coefficient is not less than  $4 \times 10^{-18} cm^2$  between 1000 Å and 910 Å. Near Lyman- $\beta$  at 1025 Å the cross-section is of the order of  $2 \times 10^{-18} cm^2$ . Using  $5 \times 10^{-19} cm^2$ , we find a unit

optical depth between 90 km and 95 km for an overhead sun. Therefore, the rate of ionization is of the order of

$$N_c(\text{U.V.}) = 0.37 \times 2.5 \times 10^7 / 7 \times 10^5 = 23 \text{ electrons cm}^{-3} \text{ sec}^{-1}$$

and is not negligible. With a recombination coefficient of the order of  $3 \times 10^{-8}$ , the electron concentration should be of the order of  $2.5 \times 10^4 \text{ cm}^{-3}$  and, of course, should be different from the X-ray ionization in the *E*-layer.

Finally, the maximum production of nitric oxide molecules occurs near the peak of the atomic oxygen concentration in the *E*-layer. Therefore, a charge transfer between atomic oxygen ions and nitric oxide molecules similar to the charge transfer between atomic oxygen ions and oxygen molecules must also be considered; it may lead to another peak of nitric oxide ions.

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## REFERENCES

- |  |      |  |
|--|------|--|
| ADEL, A.   | 1939 | <i>Astrophys. J.</i> <b>90</b> , 627   |
| BATES, D. R.   | 1952 | <i>Ann. Géophys.</i> <b>8</b> , 194  |
| BATES, D. R.   | 1954 | The Physics of the Upper Atmosphere, Chapter 12 of <i>The Solar System</i> , Vol. 2, Ed. G. P. Kuiper, University of Chicago Press |
| BATES, D. R., and MASSEY, H. S. W.                         | 1947 | <i>Proc. Roy. Soc.</i> <b>A192</b> , 1   |
| BATES, D. R., and NICOLET, M.                              | 1950 | <i>J. Geophys. Res.</i> <b>55</b> , 301  |
| BATES, D. R., and SEATON, M. J.                            | 1950 | <i>Proc. Phys. Soc.</i> <b>B63</b> , 129   |
| BATES, D. R., and WITHERSPOON, A. E.                       | 1952 | <i>M. N.</i> <b>112</b> , 101  |
| BAXTER, W. P.  | 1930 | <i>J. Amer. Chem. Soc.</i> <b>52</b> , 3920  |
| BIONDI, M. A.  | 1951 | <i>Phys. Rev.</i> <b>83</b> , 1078   |
| BURNIGHT, T. R.  | 1952 | "Physics and Medicine of the Upper Atmosphere," Chap. XIII, (Albuquerque: Univ. New Mexico Press)                                  |
| BYRAM, E. T., CHUBB, F., and FRIEDMAN, H.                  | 1954 | "Rocket Exploration of the Upper Atmosphere," Pergamon Press, London, p. 274   |
| BYRAM, E. T., CHUBB, F., FRIEDMAN, H., and GAILAR, N.      | 1953 | <i>Phys. Rev.</i> <b>91</b> , 1278   |
| BYRAM, E. T., CHUBB, F., FRIEDMAN, H., and LICHTMAN, S. W. | 1952 | <i>J. Opt. Soc. Amer.</i> <b>42</b> , 876  |
| CLARK, K. C.   | 1952 | <i>Phys. Rev.</i> <b>87</b> , 271  |
| DEB, S.  | 1952 | <i>J. Atmosph. Terr. Phys.</i> <b>2</b> , 309  |
| DITCHBURN, R. W.   | 1954 | "Rocket Exploration of the Upper Atmosphere," Pergamon Press, London, p. 313   |
| DURAND, E., OBERLY, J. J., and TOUSEY, R.                  | 1949 | <i>Astrophys. J.</i> <b>109</b> , 1  |
| FAIRE, A. C., FUNDINGSLAND, C. T., and ADEN, A. L.         | 1954 | <i>Phys. Rev.</i> <b>93</b> , 650  |
| FRIEDMAN, H., LICHTMAN, S. W., and BYRAM, E. T.            | 1951 | <i>Phys. Rev.</i> <b>83</b> , 1025   |



- GAYDON, A. G. 1944 *Proc. Roy. Soc.* **A183**, 111
- GOLDBERG, L., and MÜLLER, E. A. 1953 *J. Opt. Soc. Amer.* **43**, 1033
- HARTECK, P., and DONDER, S. 1954 *Phys. Rev.* **95**, 320
- HENRIQUES, F. C., DUNCAN, A. B. F.,  
and NOYES, W. A. 1938 *J. Chem. Phys.* **6**, 518
- HERZBERG, G., and HERZBERG, L. 1948 *Nature* **161**, 283
- HUNTEN, D. M. 1954 *J. Atmosph. Terr. Phys.* **5**, 57
- INN, E. C. Y. 1953 *Phys. Rev.* **91**, 1194
- JOHNSON, F. S., PURCELL, J. D.,  
TOUSEY, R., and WILSON, N. 1954 "Rocket Exploration of the Upper Atmo-  
sphere," Pergamon Press, p. 279
- JOHNSTON, H. S. 1951 *J. Amer. Chem. Soc.* **73**, 4542
- JOHNSTON, H. S., and CROSBY, H. 1951 *J. Chem. Phys.* **19**, 799
- JOHNSTON, H. S., and CROSBY, H. 1954 *J. Chem. Phys.* **22**, 689
- JOHNSTON, H. S., and YOST, D. M. 1949 *J. Chem. Phys.* **17**, 386
- KONDRATJEW, V. 1937 *Phys. Z. Sowjetunion* **11**, 320
- MARMO, F., ZELIKOFF, M., and  
TANAKA, U. 1952 *J. Opt. Soc. Amer.* **42**, 870
- MCMAH, R. R., and GOLDBERG, L. 1949 *Proc. Amer. Phil. Soc.* **93**, 362
- MIGEOTTE, M. 1948 *Astrophys. J.* **107**, 400
- MIGEOTTE, M., and NEVEN, L. 1952 *Soc. Roy. Sc. Liège Mémoires* **12**, 165
- MITRA, A. P. 1954 *J. Atmosph. Terr. Phys.* **5**, 28
- MITRA, A. P., and JONES, R. E. 1954 *J. Atmosph. Terr. Phys.* **5**, 104
- NEWMAN, F. H. 1935 *Phil. Mag.* **20**, 777
- NICOLET, M. 1945 *Inst. Roy. Météor*, Belgium, *Mémoires* **19**, 124
- NICOLET, M. 1948 "The Emission Spectra of the Night Sky and  
Aurora," *Phys. Soc. London*, p. 105
- NICOLET, M. 1952 *Ann. Géophys.* **8**, 441
- NICOLET, M. 1952b "Physics and Medicine of the Upper Atmo-  
sphere," Chap. XII (Albuquerque; Univ. of  
New Mexico Press)
- NICOLET, M. 1954 *J. Atmosph. Terr. Phys.* **5**, 132
- NICOLET, M., and MANGE, P. 1954 *J. Geophys. Res.* **59**, 15
- NORRISH, R. W. 1929 *J. Chem. Soc.* p. 1611
- PETRIE, W., and SMALL 1953 *Canad. J. Phys.* **31**, 911
- PIETENPOL, W. B., RENSE, W. A.,  
WALZ, F. C., STACEY, D. S., and  
JACKSON, J. M. 1953 *Phys. Rev.* **90**, 156
- PRESTON, W. M. 1940 *Phys. Rev.* **57**, 887.
- RAYLEIGH, LORD (R. J. STRUTT) 1910 *Proc. Phys. Soc.* **23**, 66
- SATO, T. 1953 *Geomag. and Geoelect.* **5**, 71
- SHAW, J. H., SUTHERLAND, G. B. M.,  
and WORMELL, T. W. 1948 *Phys. Rev.* **74**, 978
- SPEALMAN, M. L., and  
RODEBUSH, W. H. 1935 *J. Amer. Chem. Soc.* **57**, 1474
- STODDART, E. M. 1934 *Proc. Roy. Soc.* **A147**, 454
- SUN, K., and WEISSLER, G. L. 1952 *J. Opt. Soc. Amer.* **42**
- TANAKA, Y., and SHIMAZU, M. 1948 *J. Soc. Res. Inst.* **43**, 241
- TOUSEY, R. 1952 *J. Opt. Soc. Amer.* **42**, 871
- VETTER, K. 1949 *Z. Elektrochemie* **53**, 369
- WATANABE, L., MARMO, F., and  
INN, E. C. Y. 1953 *Phys. Rev.* **90**, 155
- WATANABE, K. 1954 *J. Chem. Phys.* **22**, 1564
- WATANABE, K., INN, E. C. Y., and  
ZELIKOFF, M. J. 1953 *J. Chem. Phys.* **21**, 1026

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WAIFAN, N., WALKER, W. C., and WEISSLER, G. L.	1953	<i>J. Appl. Phys.</i> <b>24</b> , 1318
WEISSLER, G. L., and LEE, Po	1952	<i>J. Opt. Soc. Amer.</i> <b>42</b> , 200
WEISSLER, G. L., LEE, Po, and MOHR, E. I.	1952	<i>J. Opt. Soc. Amer.</i> <b>42</b> , 84
WISE, H., and FRECH, M. F.	1952	<i>J. Chem. Phys.</i> <b>20</b> , 22
ZELIKOFF, M., WATANABE, K., and INN, E. C. Y.	1953	<i>J. Chem. Phys.</i> <b>21</b> , 1643
ZELIKOFF, M., and ASCHENBAND, L. M.	1954	<i>J. Chem. Phys.</i> <b>22</b> , 1680 and 1685