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ELECTRON DENSITY VARIATIONS IN WINTER

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THE ROLE PLAYED BY OZONE IN THE LOWER D-REGION

ELECTRON DENSITY VARIATIONS IN WINTER

by

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ABSTRACT

Variations in the electron densities below 70 km, measured by partial reflection experiment over Ottawa during quiet winter days, show a remarkably good inverse relationship with total ozone of previous day measured over Toronto. Meteorological transport processes as the cause of winter variability in the lower mesosphere electron density is stressed. The role of important minor neutral constituents in the ion chemistry of the lower D-region is examined in some detail and the observed variability in the electron densities well below 70 km seems to be explainable in terms of negative ion chemistry in whose reaction scheme ozone plays a decisive role through atomic oxygen. Near 70 km the negative ion chemistry alone is not sufficient to explain the results.

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THE ROLE PLAYED BY OZONE IN THE LOWER D-REGION

ELECTRON DENSITY VARIATIONS IN WINTER

1. - INTRODUCTION

Electron densities in the mid-latitude winter D-region have been known to undergo large variations from observations of "anomalous absorption" events and also from direct measurements. Its source has long been suspected to be associated with some sort of meteorological phenomenon (Dieminger, 1952) indicating a coupling between the stratosphere and the lower ionosphere. Convincing evidence for the statistical existence of such a coupling became available from the work of Bossolasco and Elena (1963) and Shapley and Beynon (1965), who showed strong relationship between stratospheric temperature and winter radio wave absorption over Europe. More extensive later works on the subject (for example, Gregory, 1965, Lauter, 1967 and Belrose, 1967) have further confirmed the existence of such an interaction and have also revealed many complexities involved in understanding the nature of this phenomenon. In particular the question of a plausible chain of cause-and-effect became debatable when correlation was also found with magnetic activity by Belrose et al (1966a) in the case of electron density data over Ottawa. In view of the recent work by Hargreaves (1973) it appears now that at least in some cases of the mid-latitude "winter absorption anomaly" there is direct influence of particle precipitation (as was also suggestive earlier from the

work of Maehlun, 1967) and that certain strong stratospheric warm-absorption events have their indirect origin in the auroral zone particle precipitation.

The greatest enhancement in the electron densities during these events take place in the 80-90 km region as shown by rocket measurements and ground based studies (Thomas, 1968, Sechrist et al., 1969), with the enhancements extending at times to the lower levels also. On the basis of the theoretical calculations on the seasonal changes in absorption carried out by Thrane, Lied and Armstrong (1973) and the calculation on the rocket electron density profiles carried out by Gellar and Sechrist (1971) it seems reasonable to believe that the immediate cause of the large enhancements in the electron densities can be attributed to the mesospheric composition changes giving rise to a reduction in the hydrated positive ion concentration and hence in the recombination coefficient. Little is known, however, regarding the winter variability in the lower mesosphere, namely below 70 km, where the interaction with the stratosphere should be more directly observable. This is mainly due to the fact that the conventional techniques of measurements for obtaining continuous stretch of data are generally sensitive to the state of ionization above this altitude.

Attention was first draw by Belrose et al (1966b) to the presence of large day-to-day variability in the lower D-region electron

density during quiet winter days, using the electron density data measured by partial reflection experiment over Ottawa. The relationship between this type of variability and those associated with the interrelated group of events mentioned above, namely, stratwarm, magnetic activity and ionospheric absorption, is not yet known. While it is admitted that at present no sufficient electron density data is available in this height region to enable a classification of this variability, we are of the opinion that probably this is not always related to the circumstances leading to the "anomalous absorption" events. In interpreting their results Belrose et al (1966b) had invoked the importance of ozone in the D-region morphology. However no specific conclusion regarding the influence of ozone on this variability has yet been established.

Recent developments in the D-region ion-chemistry and, in particular, the very significant role played by ozone in the reaction scheme for the minor atmospheric constituents prompted us to reexamine the relationship between the winter variability in the lower D-region electron density and the corresponding variability in the total ozone. Further an examination of the relationship between the total ozone and the ozone concentration at higher levels as deduced from Umkehr measurements showed very good correlation in the case of temperate latitude stations (Angreji, 1967) which implied that any possible changes in the total ozone produced by meteorological factors will be experienced at higher levels as well. The present study shows that there is a remarkably good dependence of

electron densities below 70 km on the total ozone content in the atmosphere. Furthermore, there is positive evidence that the atmospheric circulation and the resulting transport of ozone-rich regions are important factors in the winter electron density variability below 70 km.

2. -- THE OBSERVED RELATIONSHIP BETWEEN TOTAL OZONE AND ELECTRON DENSITY

For the purpose of the present study we have used electron density data below 70 km measured by the partial reflection technique by Belrose et al (1966b) as presented by them for 5 magnetically quiet days in December 1961 and also the data presented by Belrose and Bourne (1967) in the form of average electron densities of the 5 quietest days in a month for 4 winter months during 1961 and 1962. A further comparative study was made using A_x/A_0 ratio for December 1969 and January 1970 taken from Belrose (1973). The total ozone data used are those measured over Toronto during the same period and taken from the World ozone data publication bulletin (published by The Department of Transport, Meteorological branch, Toronto, 1961, 62, 69 and 70).

Fig. 1 shows several plots of electron densities on individual quiet winter days during December 1961 for 52 km, 60 km and 70 km over Ottawa against the total ozone over Toronto. The first plot in each of the sections, (a), (b) and (c), of the figure represents the relationship between the electron density and the total ozone of the same day. As seen in the figure no correlation between the two parameters is present. The second plot where-in we have related the electron density

on a given day with the total ozone of the next day also shows no relationship between them. When the electron density was plotted against the total ozone of the previous day as shown in the third column, a clear correlation between the two parameters in the form of an inverse dependence between electron density and ozone emerged at all the three heights. The regression lines shown have correlation coefficients, 0.87, 0.97 and 0.75 for 52 km, 60 km and 70 km respectively. (It may be mentioned that the one point shown encircled in fig. 1 (a) was obtained after extrapolating the electron density from 54 km down to 52 km). Further examination of the figure shows that the slope of the best fitting line is the smallest at 52 km and increases with height up to 70 km, which means that the variation in electron density with the variation in total ozone tends to become larger as we go from 52 km to 70 km. However this dependence becomes less clear near 70 km (a plot for 75 km did not show any correlation) as seen by the increase in the degree of spread of points, suggesting that it will be difficult to observe any dependence between electron density and ozone at altitudes above 70 km, probably because of the decrease in the concentration of ozone in relation to other minor constituents which principally control the equilibrium densities at those heights.

In Fig. 2 we have plotted the averages of the electron densities representing 5 magnetically quiet days in a month for four winter months in 1961 and 1962 against the total ozone. The total ozone of a day previous to the quiet day was used to obtain the average values because here

again we found that no correlation emerged for the other two cases considered in Fig. 1. It may be noticed that the slopes of the regression lines are approximately the same for all the three heights considered, namely, 55 km, 60 km and 70 km. It should be commented however that the ozone value near 290 units represents the average of only two days for which data were available and the value near 345 units is an average of only four days as one of the days was excluded because of a stratospheric warming event which was in progress in late January 1962 (it is likely that during a warming event the presence of several other atmospheric changes might conceal any direct relationship between ozone and electron density). Further the data presented in this figure represents two winters and the possible changes in the mesospheric conditions during the period of one year might somewhat alter the degree of dependence between the two parameters. Considering these factors an inverse relationship between electron density and total ozone is evident in this figure also.

A particularly significant feature which emerges from Figs. 1 and 2 is the fact that we found good correlation between electron density and ozone when we plotted the former against the previous day's ozone values. This appears to suggest that the part played by transport processes is very important in determining the electron densities over a given location. We repeated the plot in Fig. 1 by taking the two parameters with ± 2 days time delays between them. But none showed any correlation suggesting that a definite velocity is involved in the

mechanism by which ozone-rich regions are transported. Considering the geographical separation between Toronto and Ottawa (3.7° in longitude and 1.8° in latitude), the time delay of approximately one day appears to be consistent with the passage of a baroclinic wave moving at a rate of approximately 500 km per day in a westerly flow. For further verification of this aspect it will be desirable to have both these parameters measured over more than two locations.

On the basis of Figs. 1 and 2 one might expect the total ozone to be correlated also with other ionospheric parameters representing electron density in this height region. The ratio of the extra-ordinary to ordinary amplitude, A_x/A_o , of the partially reflected signals is a measure of the integrated differential absorption or the average electron density below the reflection level. A plot of this parameter at 2.66MHz corresponding to a reflection height of 76 km (Belrose 1973) against the total ozone is presented in Fig. 3a. The period considered here is December 1969 and January 1970 being the quietest in seven winters, with little storminess and no clear cut magnetic storm after effect in the D-region ionization. Some explanation is due before interpreting the figure. In winter the contribution from above 70 km to the total differential absorption below 76 km is considerable compared to (and some times exceeds) the contribution from below 70 km. Further in Fig. 1 we noted a trend for the electron density vs total ozone correlation to become worse near and above 70 km. Therefore a dependence of A_x/A_o on total

ozone will be readily observable only if (a) the differential absorption variations are themselves well correlated at all the heights below 76 km or (b) if they are present mainly below 70 km. This aspect is illustrated in Fig. 3b showing the relationship between the total ozone and the total differential absorption at 2.66 MHz calculated below three assumed reflection heights, 60 km, 70 km and 76 km using the same electron density profiles as were used in Fig. 1. The progressive deterioration in their relationship with increasing altitude is obvious and corresponding to 76 km the correlation is indeed poor. This is due to the lack of correlation mentioned as (a) above. The result in Fig. 3a thus suggests that probably the variations at upper levels were significant enough to mask those produced by ozone at lower levels during the general period considered in the figure. However there seems to be some trend for an expected positive correlation if we restrict to only few consecutive days as indicated by the filled-in circles which represent the data for 5, 6, 7, 8, and 9 January 1970 (it may be noted that in this figure the two parameters correspond to the same day; plots with time delay between them either showed less correlation or did not improve the correlation at all). In any case since the winter variability in the lower D-region electron density produced by ozone need not be correlated with upper level variation (as for example, the profiles of Belrose et al, 1966 indicate) the parameter A_x/A_0 corresponding to higher reflection levels need not always show the kind of correlation expected on the basis of Figs. 1 and 2.

3. - INTERPRETATION OF THE RESULTS

Under "quiet" conditions (namely, when the rate of production does not change) the electron density variability in the lower D-region could be produced either by a change in the negative ion concentration determined by the rate of attachment and detachment processes or by a change in the recombination rate depending upon the positive ion composition. We have noted above the possible significance of the latter process in the explanation of the electron density variations associated with the winter "anomalous absorption" events (Thrane, Lied and Armstrong 1972). In the present case, since we are concerned with the region below 70 km, where the role of negative ions become increasingly important, we will attempt an interpretation of the results mainly by examining the part played by ozone in the negative ion chemistry through direct and indirect reaction schemes. We will then deduce an expected relationship between the ozone concentration and the electron density at various levels and discuss them in relation to the observation.

The general relationship between the electron density, N_e , and the negative ion to electron density ratio, Λ , can be written as:

$$N_e = (Q/\alpha)^{1/2} \left\{ (1+\Lambda) \left[1 + (\gamma/\alpha)\Lambda \right] \right\}^{-1/2}$$

Below 65 km the ion production rate Q is mainly due to cosmic-rays. This

contribution is only approximately 25 percent of the total production near 70 km, the remaining being due to Lyman α and to some degree X-rays with wavelength less than $3 \text{ \AA}$. γ is the coefficient for charge neutralization between positive ions and negative ions and is assumed to have a height-independent value of $10^{-7} \text{ cm}^3 \text{ sec}^{-1}$. α is the recombination coefficient for electrons with positive ions. Little is known about its value below 70 km. In the region between 70 km and 82 km the work of Reid (1970) has shown large values (up to $5 \times 10^{-5} \text{ cm}^3 \text{ sec}^{-1}$) which are believed to be due to the presence of large concentration of hydrated positive ions at these heights. The rapid rate of decrease in α above 82 km seen in Reid's results is believed to be due to a corresponding rate of disappearance of water vapour at these altitudes. A decrease in α observed below 75 km seems to be due to a different cause. Turco and Sechrist (1970) has extrapolated Reid's values at 70 km down to 50 km, according to which we have assumed here that α varies from $10^{-5} \text{ cm}^3 \text{ sec}^{-1}$ at 70 km to $5 \times 10^{-6} \text{ cm}^3 \text{ sec}^{-1}$ at 50 km. The above equation can be simplified further into forms appropriate for the three heights as follows:

$$N_e = (Q/\gamma)^{1/2} \Lambda^{-1} \quad (\text{near 50 km}),$$

$$N_e = (Q/\alpha)^{1/2} \left\{ \Lambda [1 + (\gamma/\alpha)\Lambda] \right\}^{-1/2} \quad (\text{near 60 km}), \text{ and}$$

$$N_e = (Q/\alpha)^{1/2} (1+\Lambda)^{-1/2} \quad (\text{near 70 km}).$$

Under quiet conditions Q can be considered constant particularly below 65 km. (The values of Q used here are 0.5, 0.18, and 0.39 ion-pairs cm^{-3} for 50 km, 60 km and 70 km respectively. These are based on the cosmic-ray production rate given by Webber (1962) for solar minimum conditions, ionization calculated according to the X-ray spectrum for nonflare conditions given by Pounds (1970) and that calculated using a Lyman α flux of $4.3 \text{ ergs cm}^2 \text{ sec}^{-1}$ given by Weeks (1967) for near solar minimum conditions). It can be seen therefore that near 50 km the electron density variations are due only to Λ (note the absence of α in this equation) and is in an inverse sense. At higher levels this dependence becomes less marked as illustrated in Fig. 4a. It may be noted further that at 70 km the value of Λ is very small and so is the dependence of N_e on Λ .

In order to study the dependence of Λ on ozone and other important minor constituents we adopted the negative ion reaction scheme given by Reid (1970) which included O_2 , O , O_3 , NO , NO_2 , CO_2 and $\text{O}_2(^1\Delta)$. Calculations performed by including OH , H_2O and N in the reaction scheme did not show any difference large enough to be of consequence for our discussion. The concentration of these various constituents used are the same as those tabulated by Turco and Sechrist (1970) except the NO concentration which we adopted from Meira (1971) (after extrapolating Meira's values downward using the theoretical height profile of Shimazaki and Liard (1970). It should be mentioned that in a

study where the dependence of Λ on a test constituent is investigated it is necessary also to include in the calculation a provision for simultaneous changes in the concentrations of other constituents caused by the assumed changes in the test constituent concentration. The test constituent in the present case being O_3 , the changes in its concentration could produce corresponding changes in mainly $[O]$, $[NO]$, $[NO_2]$ and $[O_2(^1\Delta)]$ in varying degrees. Consideration of the various neutral reaction schemes involving these constituents shows that $[O]$ is inversely related to $[O_3]$ and so is the dependence between $[NO]$ and $[O_3]$ but at much less reduced rate (see the appendix). A preliminary calculation showed that the Λ dependence on $[NO_2]$ was insignificant and that the dependence on $[O_2(^1\Delta)]$ was very small (as will be shown in Figs. 5a, b and c).

The calculation of Λ dependence on the test constituent was carried out therefore by keeping the product $[O][O_3]$ always a constant whenever $[O_3]$ was changed, the dependence on other constituents being studied by simply repeating the calculation for various values of their concentrations. The results of the calculation are shown in Figs. 5a, b and c, for 51 km, 60 km and 70 km respectively. The curve labelled $\Lambda(O_3, 0)$ represents the Λ dependence on $[O_3]$ or the ratio $[O_3]/[O]$ when the product $[O][O_3]$ is constant, and this dependence is the largest at all the heights. It is interesting to note that a wide range of variation in $[O_3]$ alone (keeping $[O]$ constant which, however, is unrealistic) does

not have any appreciable influence on Λ (the curve labelled $\Lambda(O_3)$), which implies that $\Lambda(O_3, 0)$ dependence is produced principally through the dependence of $[O]$ on $[O_3]$ (therefore a curve $\Lambda(O)$ to represent the relationship between Λ and $[O]$, keeping $[O_3]$ a constant, would be almost identical to the $\Lambda(O_3, 0)$ curve. This calculation has not been carried out). A further point of interest to be noted in these figs. is that there is a limiting value for the ratio $[O_3]/[O]$ above which the variation in Λ is very small and at 51 km this value is close to that corresponding to the ambient densities of these constituents (as per the reference cited above and marked on the horizontal axis) whereas it is further away from the assumed values at higher levels.

The curves of Fig. 5a, b and c and those in Fig. 4a were used together to obtain the results presented in Fig. 4b which represent the relationship between N_e and $[O_3]$. An inverse relationship between them is immediately evident at all the heights in agreement with the observational results. Further the slopes of these curves seem to be dependent in varying degrees on the ratio $[O_3]/[O]$ at these heights. Considering first 51 km and 60 km, this dependence seems to be more marked at 51 km than at 60 km, suggesting thereby that the different slopes of the N_e vs total ozone curves in Figs. 1 and 2 could be due to the $[O_3]/[O]$ ratios which were present at these levels at the time of the observation. This explanation, however, is based on the assumption that the changes in the mesospheric ozone concentration are directly related to the changes in the total ozone (we shall return to this point again).

At 70 km the slope of the N_e vs $[O_3]$ curve is much less significant than at the lower levels, which being different from the observed trend, seems to pose a problem for an interpretation similar to that applicable for the lower altitudes. This is due clearly to the relatively small role of Λ (and increasingly important role of α) at these levels and thus appear to point out some insufficiency in an interpretation based only on the negative ion chemistry. It might be worth while therefore to visualize the consequence of possible changes in the positive ion composition (and hence in the recombination coefficient). If we assume that significant variations in the atomic oxygen density is associated with the changes in the ozone concentration in an inverse sense (as described earlier) and if the hydrated positive ionic species play a significant role at these heights, then a proportional dependence between $[O_3]$ and the recombination coefficient can be expected because of the role of atomic oxygen in short circuiting the positive ion reaction chain leading to the formation of the hydrated ions as described, for example, by Narcisi et al (1972). Under these circumstance an inverse relationship between $[O_3]$ and N_e can be obtained. Yet another possibility could be the presence of an inverse variation with $[O_3]$ of $[NO]$ (which might gain significance at these levels) whose contribution to the electron production through Lyman α radiation gains importance over cosmic-ray ionization near this height. A more detailed discussion of these various aspects will be pursued in a separate work.

An additional point to be noted from Figs. 1 and 2 and

the Fig. 4b is that the calculated values of electron densities at 51 km and 60 km are considerably smaller than the values measured by partial reflection experiment. There are several factors which could contribute to this disparity. Of those which are considered in our calculation, the ones to which the electron density is most sensitive are the ion-production rate, the ratio $[O_3]/[O]$ and the NO density. Since the ion production rate due to the galactic cosmic-rays is a better known parameter a large discrepancy due to this is very unlikely. Quantitative considerations show that a drastic reduction in $[O_3]/[O]$ (approximately four orders of magnitude) is required to remove this discrepancy, which is also unlikely judging from the several experimental determinations and theoretical calculations of the day time $[O_3]$ (for example, Anderson et al, 1969, Hunt, 1966). The good degree of Λ dependence on $[NO]$ seen in Fig. 5 might suggest that the range of $[NO]$ values used in our calculations is somewhat overestimated in view of the fact that very little is known about the NO concentration below 70 km. However a very significant (and perhaps the most significant) contribution to the discrepancy could arise from the fact we have not included in our calculation any provision for electron detachment from NO_3^- ions. Photo-detachment of this terminating ions and some others has been suggested by Thomas et al (1972) to be the chief source of electrons below 70 km. A detailed investigation into these various aspects is also being pursued. Our present calculation serve to illustrate only that the observed dependence of N_e on total ozone is similar to what one would expect

according to the reasonably known negative ion-chemical reaction schemes for the height region where Λ plays a major role in determining the electron density.

4. - DISCUSSION ON THE RELATIONSHIP BETWEEN TOTAL OZONE AND MESOSPHERIC OZONE CONCENTRATION

We mentioned before that a good correlation existed between total ozone and the high altitude ozone concentrations deduced from Umkehr observations over a temperate latitude station. (Angreji, 1967, the study was carried out for Tateno, Japan) which indicated that any change in the total ozone produced by meteorological processes could be experienced at higher levels also. Such a clear correlation could not be obtained for Arosa, Switzerland, located in middle latitude. In this connection it should be pointed out that there is a dependence of total ozone and high altitude ozone concentration on K_p which increases with latitude (Angreji, 1967). This would imply that at middle and higher latitudes a considerable change in $[O_3]$ on upper layers takes place due to particle effects which would be sufficient to conceal any direct relationship between high altitude ozone and total ozone caused by meteorological changes. Only an analysis during the quietest days can bring out this relationship for middle and higher latitude stations. The results for temperate latitude stations are therefore sufficient to indicate the general association that exists between total ozone and the ozone at

higher levels.

5. - CONCLUSIONS

From the present study on the role played by ozone in determining the lower D-region electron densities in winter we derive the following conclusions:

1. There is a clear inverse relationship between total ozone and the electron densities in the height region from 52 km to 70 km and the degree of this relationship could vary with height.
2. The winter variability in the mesospheric electron densities may be caused by a meteorological circulation process by which ozone - rich regions are transported, indicating that ozone plays a direct role in the coupling between the lowest part of the ionosphere and the upper stratosphere.
3. For altitudes well below 70 km the variations in $[O_3]/[O]$ ratio seem to explain the observed inverse relationship between electron density and total ozone. This is because of the decisive role played by ozone through atomic oxygen in the negative ion chemistry.
4. The behaviour near 70 km does not seem to be

explainable in terms of the negative ion chemistry. It seems to suggest a proportional change in the electron loss coefficient or an inverse variation in $[NO]$ or both taking place in association with the variation in the lower mesospheric ozone concentration or in total ozone.

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APPENDIX

INTERDEPENDENCE BETWEEN $[O_3]$ AND OTHER MINOR CONSTITUENTS CONCENTRATIONS THAT ARE IMPORTANT IN THE NEGATIVE ION CHEMISTRY

The most important of the minor constituents considered in the negative ion reaction scheme whose concentrations depend upon $[O_3]$ are O, NO, NO_2 and $O_2(^1\Delta_g)$. Their interdependence is considered below in some detail. The relationship between $[O_3]$ and $[O_2(^1\Delta_g)]$ was not studied because the Λ dependence on the latter is very small. All the reactions involving various constituents as tabulated by Turco and Sechrist (1970) were considered and the more important ones were selected after evaluating the relative contribution of each of them for the height region 50-70 km using a typical winter temperature profile. Writing down the continuity equations for $[O]$, $[O_3]$ and $[NO]$ separately, assuming equilibrium and then eliminating terms that are common among them, the following relationships can be obtained.

$$[O] = \frac{2 J_2 I_2 [O_2] - [O_3] \left\{ k_7 [NO] + k_9 [OH] + k_8 [H] \right\}}{2 k_2 [O_3] + k_5 [NO_2]}$$

and,

$$\frac{[NO]}{[O]} = \frac{k_5 [NO_2]}{k_7 [O_3]}$$

where, k_2 , k_7 , k_8 and k_9 are the rate constants for the reactions of O_3 with O, NO, H and OH respectively, k_5 corresponds to the reaction of O with NO_2 , J_2 is the rate constant for the photo-dissociation of O_2 due to $\lambda < 2424 \text{ \AA}$ and I is the corresponding intensity.

In the first of the two equations the first term in the numerator is greater than the sum of the other terms by approximately 10 - 100 times and in the denominator the first term is larger than the second by approximately 10 - 1000 times as we go from 50 to 70 km. Thus an inverse relationship between $[O]$ and $[O_3]$ is apparent when production term is constant. Regarding the second equation a term $k_6 [O] [M]$ should be added to the denominator on the right hand side for altitude above 65 km. We can use this relation to assess the degree of variation in $[NO]$ compared to $[O]$ for a given change in $[O_3]$, based on the following reasoning.

The rate of formation of $[NO_2]$ from the reaction, $NO + O_3 \rightarrow NO_2 + O_2$, proceeds at almost comparable rate as the formation of $[NO]$ back from the reaction $NO_2 + O \rightarrow NO + O_2$. As a result if $[O]$ does not change due to other reasons, a change in $[O_3]$ alone may not alter $[NO_2]$ significantly. However, since in practice, an increase in $[O_3]$ causes a corresponding decrease in $[O]$ (and vice-versa), the rate of formation of $[NO]$ from $[NO_2]$ becomes retarded causing a net build up in $[NO_2]$. The percentage change in $[NO_2]$ might tend to be very large because of

its smaller ambient density causing the ratio $[NO_2]/[O_3]$ to grow larger. (using standard values for the rate coefficients and number densities we can show that an increase by a factor of 2 in $[O_3]$ can cause $[NO_2]$ to build up at a rate of approximately 15 percent per second. Detailed calculation on the equilibrium value of $[NO_2]/[O_2]$ have not been done. However it is expected to be large). According to the second equation then, the ratio $[NO]/[O]$ should also be proportionately increased. But since $[O] \propto 1/[O_3]$ it follows that under equilibrium conditions $[NO]$ must decrease at a much smaller rate than $[O]$ for a given increase in $[O_3]$. Because of the preponderance of $[O]$ over $[O_3]$ the above equation does not indicate the dependence of $[O_3]$ on $[NO]$ near and above 70 km.

FIGURE CAPTIONS

- Fig. 1. The electron density values over Ottawa measured by Partial reflection technique (Belrose et al., 1966b) for the 5 magnetically quiet days in December 1961 vs total ozone over Toronto, plotted for the three cases described in the text (a), (b) and (c) are for 52 km, 60 km and 70 km respectively.
- Fig. 2 The electron density averages over Ottawa (Belrose and Bourne, 1967) representing 5 quietest days in a month for four winter months, Nov. 61, Dec. 61, Jan. 62 and Nov. 62, plotted against the average values of total ozone (of a day previous to the quiet day) over Toronto (a), (b) and (c) are for 55 km, 60 km and 70 km respectively.
- Fig. 3 The A_x/A_0 ratio corresponding to the signals partially reflected from 76 km over Ottawa for Dec. 1969 and Ja. 1970 (taken from Belrose 1973) plotted against the corresponding ozone values over Toronto.
- 3b. Total differential absorption below three assumed heights ie, 60 km, 70 km and 76 km, calculated using the same electron density profile as used for Fig. 1, plotted against the total ozone, to demonstrate the progressive deterioration of the correlation with altitude.
- Fig. 4a. Variations in electron density with λ according to the relationship given in the text for the three heights, 51 km,

60 km and 70 km.

- 4b. Variations in electron density with simultaneous changes in $[O_3]$ and $[O]$ obtained using the results in 4(a) and Figs. 5(a), (b) and (c) plotted for the three heights.

Fig. 5(a), (b) and (c). Dependence of Λ on important minor atmospheric constituents namely, O_3 , O , NO and $O_2(^1\Delta_g)$ calculated according to the negative ion reaction scheme of Reid (1970) plotted for 51 km, 60 km and 70 km respectively.

DECEMBER 1961

NOV' 61
DEC' 61
JAN' 62
NOV' 62

fig 2

TOTAL OZONE OVER TORONTO (mAT CM)

[O]

10^{11}

10^{10}

10^9

51 KM

10^6

10^5

Λ

$\Lambda(\text{NO})$

$\Lambda(\text{O}_3, \text{O})$

$\Lambda(\text{O}_3)$

$\Lambda(\text{O}_2^+ \Delta)$

10^4

10^3

10^{10}

10^{11}

[O₂⁺Δ]

10^8

10^9

[NO]

10^{10}

10^9

10^{10}

10^{11}

10^{12}

[O₃]

[O]

10^{12}

10^{11}

10^{10}

10^4

60 KM

$\Lambda(O_3, O)$

10^3

$\Lambda(O_2^1 \Delta)$

$\Lambda(O_3)$

Λ

10^2

$\Lambda(NO)$

10^1

10^{10}

[O₂¹Δ]

10^{11}

10^8

[NO]

10^9

10

10^8

10^9

10^{10}

10^{11}

[O₃]

240, 1977