

Progress in Atmospheric Chemistry over the Last 50 Years

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An account of the progress of research on atmospheric chemistry in the last 50 years in the context of Indian activities is presented. Three separate phases are discussed. The first phase was concerned with the studies in the 30's to 50's on the origin, stratification and distribution of ionospheric ionization. The second phase started with the observations with rockets and satellites, during and after the IGY and consisted of measurements on ion composition in the ionosphere and the ion chemistry developed to explain the preponderance of NO^+ ions in the E and F regions and the water cluster ions in the D region. The third phase began in the 70's when the question of depletion of stratospheric ozone by human activities was brought up.

1 Introduction

The starting point in atmospheric chemistry centres on the two classic works of Sydney Chapman^{1,2}: the first in 1930 describing the simple chemistry of ozone formation and destruction in the atmosphere and the second in 1931 providing the basis for the production and distribution of electrons in the upper atmosphere as a result of interaction of incoming solar radiation and the distribution of ionizable constituents. Shortly thereafter in a series of papers that came out of Calcutta University, Calcutta, Bhar³ and Mitra *et al.*⁴ went into the question of the origin and stratification of the E and the D regions using Pannekoek's methodology⁵ (which actually preceded Chapman's) to remove the restriction of monochromatic radiation inherent in the Chapman theory, and introduced the concept of total dissociation of O_2 above 100 km. In the 50's as estimates of recombination coefficient showed variations with height and with time, another restriction of Chapman's theory—that the loss coefficient is constant with height and time—was removed, and resulting modifications in ionization structures were examined by a number of scientists, principally Nicolet⁶, Gledhill and Szendrei⁷ and Mitra^{8,9}.

The second phase began with the IGY which saw the emergence of a new area: "Ion Chemistry". The unexpected dominance of NO^+ ions over much of the ionosphere prompted examinations of reactions that would generate NO^+ ions from the initially produced O_2^+ , N_2^+ and O^+ ions and measurements of appropriate reaction rates in the laboratory. Measurements of such ion composition continued later with satellite-borne sensors at various height ranges and under various conditions (day and night, polar cap absorption events, auroral phenomena, solar eclipses, etc.). Sub-

sequently, in an effort to adequately match the observed ion composition values with those calculated *ab initio* with laboratory values of the reaction rates, simultaneous measurements of both neutral and ion composition were undertaken.

The third phase began with the suggestion in early 70's that radicals like NO_x injected into the atmosphere by supersonic aircrafts could alter the ozone environment. Then followed a series of suggestions relating possible ozone depletion due to a number of radical species, primarily NO_x , HO_x , and ClO_x arising from both natural and human activities; the natural sources being primarily soil, volcanic eruptions, solar proton events and the human activities covering biomass burning, aerosol sprays and supersonic flights. During the following decade a series of intensive investigations began simultaneously on a number of fronts: measurement of the interacting minor species as functions of height, laboratory measurements of the reaction rates of the key reactions particularly those involving catalytic destruction of ozone by ClO , OH and NO_x and the partitioning reactions that divert the catalytic agents into reservoir species; and modelling efforts to reproduce observed distributions. Most models predicted a column change of no more than a few per cent in ozone during the last decade from human activities. This picture changed dramatically with the recent discovery of an extensive severe "ozone hole" in the Antarctic, first announced by British scientists over Halley Base and subsequently confirmed by US satellite observations (taken earlier) and also by balloon observations over the Japanese Base Syowa for about two decades.

The gradual shifting of interest with time from one level to another and in the nature of the problem is shown in Fig. 1.

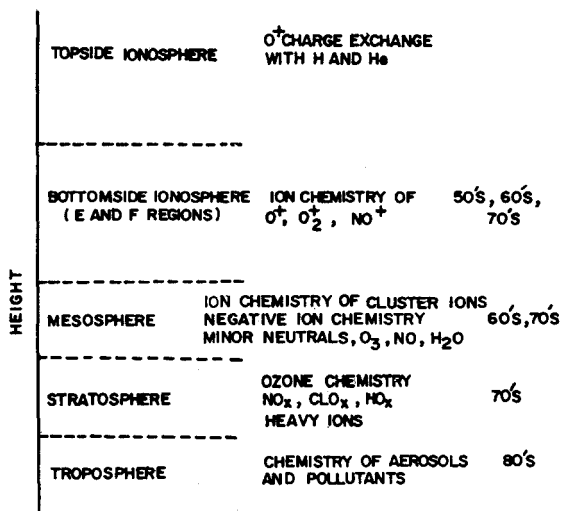
2 Research on Ionospheric Formation and Layering: 1930-1960 (Phase I)

The classic work of Chapman on the formation of an ionization layer makes a number of assumptions, the most important being that: (a) radiation is monochromatic, (b) the loss processes are uniform over the region, and (c) constituents are N_2 and O_2 in undissociated form. Such a concept, of course, provides the formation of one layer only and consequently, while a layering at F region height was indicated, there was for several years a controversy regarding the origin of the E region. This difficulty of providing another layer at E region heights led to the suggestion of a non-radiation origin for the E region, viz. bombardment by neutral corpuscles emitted by the sun. However, the Indian group (Bhar³, in particular) showed that a separate layer is possible if one discarded the concept of monochromatic radiation and introduced an atmosphere in which O_2 is completely dissociated in the region 80-130 km. In this approach they used the for-

mulation of Pannekoek, which has been one of the earliest approaches in the treatment of ionization in the upper atmosphere.

The question of dissociation of O_2 in the region 80-130 km had already been attacked by other Indian scientists, notably Majumdar¹⁰ and Mitra and Rakshit¹¹. The assumed distributions of neutral constituents are given in Table 1. The other important concept that they brought in was a relatively higher temperature in the upper atmosphere than in the lower, although the value of 600 K for regions in F region heights will now be considered too low. Another major departure from Chapman theory was the introduction of non-monochromatic nature of radiation: Bhar brought in the concept of ionization not by single wavelength but ranges of wavelengths appropriate for the ionizable constituents N_2 , O_2 and O , that had then been collected by Saha¹² and Chapman and Price¹³. The resulting ionization worked out by Bhar³ and given in Fig. 2, provides several ionization maxima: one at 250 km due to atomic oxygen, the second at 160 km due to N_2 and the third at 90 km due to O_2 . Bhar identified the three maxima with F2, F1 and E1 regions.

Further steps came in the 40's and 50's through a variety of approaches: (a) by looking afresh into the question of layer formation in the context of new information on solar radiation (which came to be available from rocket measurements after World War II), (b) through exhaustive examination of the electron loss processes, and (c) from a study of the variations in atmospheric temperature. Around this time came a series of studies by Massey and Bates¹⁴ on the processes of electron and ion losses. These brought out the importance of the negative ions of the lower ionosphere, and possible roles of temperature and pressure in the variation of the effective recombination coefficient (α) in the upper regions of the ionosphere. They introduced the following expression which was used for years to come:



DIAGRAMMATIC REPRESENTATION OF DIFFERENT CHEMICAL REGIONS

Fig. 1—Diagrammatic representation of different chemical regions and indication on the shifting of interest in the last five decades

Table 1 – Distribution of Neutral Constituents

Region	Mean Temperature (T)	Constituents	Density distribution
80 to 130 km	300	O N O	$O_2:N_2 = N_0 e^{-\theta z}$ $N_0 = 1.6 \times 10^{14} \text{ cm}^{-3}$ $\theta = 4.6 \times 10^{-6}$ Datum level: 80 km
130 km upwards	600	O N	$N_z = N_0 e^{-mgz/kT}$ $N_0 = 4 \times 10 \text{ atoms/cm}^3 : O_2$ $= 1.6 \times 10^{12} \text{ molecules/cm}^3 : N_2$ Datum level: 130 km

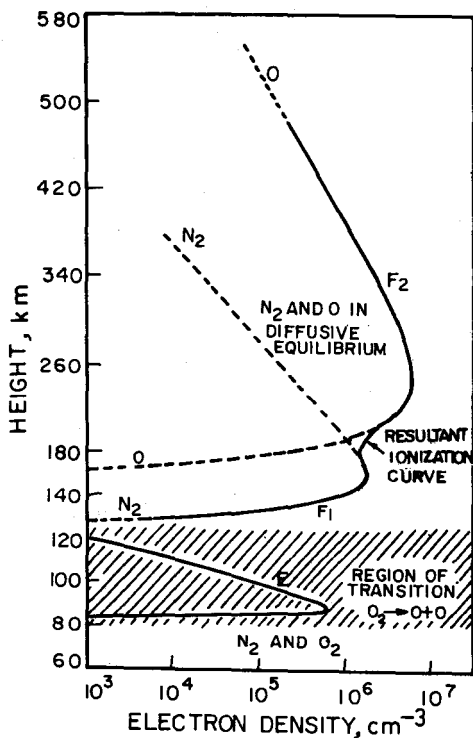


Fig. 2—Ionospheric stratification calculated by Bhar³

$$\alpha = \alpha_e + \lambda \alpha_i + \frac{1}{N_e T} \frac{dT}{dt} + \frac{1}{N_e (1 + \lambda)} \frac{d\lambda}{dt}$$

and

$$\lambda = \frac{\beta N_e N - [N_e (1 + \lambda)] (d\lambda/dt)}{\rho N_e + K N_e N + q + (\alpha_i - \alpha_e) N e^2}$$

where

- N_e Electron density
- N Density of neutral particles
- α_e Electronic recombination coefficient
- α_i Ions recombination coefficient
- β Radiation attachment
- q Rate of ion production
- ρ Coefficient of photodetachment
- K Coefficient of collisional detachment

A series of works in different parts of the world looked for changes in the recombination coefficient in both E and F regions by using the diurnal variations of f_0E and f_0F2 . Baral and Mitra¹⁵ obtained a very large seasonal variation (for nighttime conditions) for the F region as a function of season. Changes in temperature (and of scale height) with height and with time were observed. It was clear that these changes in α and H should be incorporated in calculating the ionization distribution function. A series of such works followed. Mitra⁸ considered the variations of temperature and recombination coefficient with height for

the D layer, Pfister¹⁶ for the E layer, and Bates and Massey¹⁷ and later Bates¹⁸ considered the effect of the variable recombination coefficient on the F layers. Gledhill and Szendrei⁷ considered mathematically the effect of the linear temperature gradient on an otherwise Chapman layer, and Nicolet⁶ considered the effects of both recombination coefficient and temperature on the layer produced by a band of solar ultraviolet radiation. These works materially advanced our concept on the ionization distribution. A further improvement was introduced by Mitra⁸ in which he derived general formulae for calculating the height distribution of ionization taking into account the possible variabilities of H (i.e. temperature and molecular composition) and of α and then by consolidating the available experimental data regarding the nature of variations of α with height and time, obtained height distribution of ionizations in the D, E, F1 and F2 regions in one consolidated attempt. In this work the basic variations used were:

$$H = H_0 + ah$$

$$\alpha = \alpha_0 f(v, p, T)$$

An important conclusion was the possibility of a simple Chapman layer (which may be identified with the F1 region) bifurcating, as it were, into two regions—F1 and F2—mainly as a result of the height gradient of the recombination coefficient. Whether or not the region bifurcated depended on the nature of the height gradient of the scale height and recombination coefficient, the form for the function f determining the variation of α with height was found to be important.

One of the representative results of this bifurcation phenomenon as obtained by A P Mitra is shown in Fig. 3. The main point in his calculations was that bifurcation occurred—giving *two* distinct maxima, one at or near the level of maximum ion production and another higher up—if the recombination coefficient is decreasing with height or when the recombination coefficient is decreasing and the scale height increasing with height.

It was also a period when substantial progress was made in the understanding of the complex processes contributing to the effective recombination coefficient α . Estimates of the recombination coefficient made by a number of investigators including Indian workers clearly showed that the nature of these processes has to be quite different at different levels of the ionosphere: the value of α changes from around $10^{-5} \text{ cm}^3 \text{ s}^{-1}$ at 60 km to about $10^{-11} \text{ cm}^3 \text{ s}^{-1}$ at 300 km (a decrease by six orders of magnitude). A comprehensive model covering the heights from 60 to 500 km was first provided by Mitra⁸ and is shown in Fig. 4: this

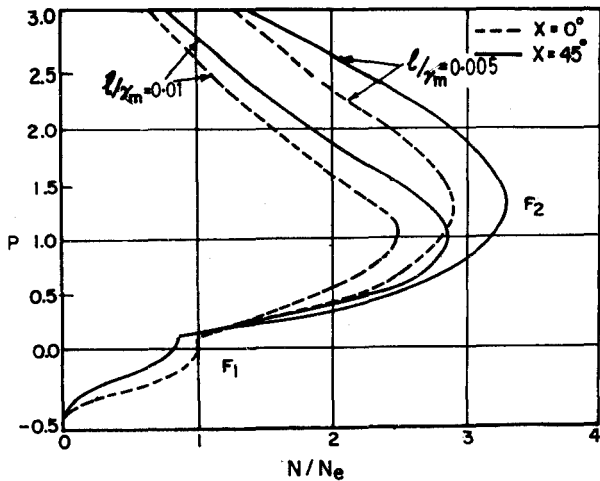


Fig. 3—An example of bifurcation in the F-region as a result of height variations in recombination coefficient and scale height

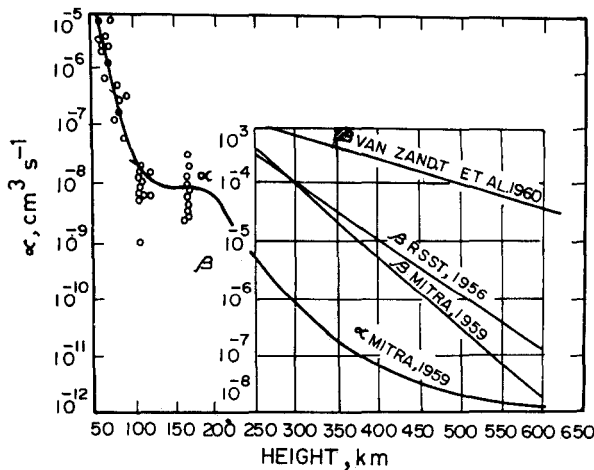


Fig. 4—A consolidated view (after Mitra) of the effective recombination coefficient from 60–600 km

was widely used in the succeeding years with occasional modifications.

Since no single process could be assumed to cover such a wide range of altitudes, Mitra considered several processes: processes involving negative ions (and expressed by the parameter $\lambda\alpha_i$, λ being the ratio of the concentrations of negative ions and electrons and α_i being the coefficient of recombination between positive and negative ions), dissociative recombination processes (expressed by α_D and applicable only to molecular ions), and atom-ion interchange processes (such as those that convert the atomic ions to molecular ions, which then go through dissociative recombination). As the first step, he selected the most dominant process or processes for different height regions and generated or used experimental data that would relate to specific coefficients for these height regions. His classification of the ionospheric regions in terms of the dissipation processes is shown in Fig. 5. He pointed out that as we go from 60 km to 600 km we

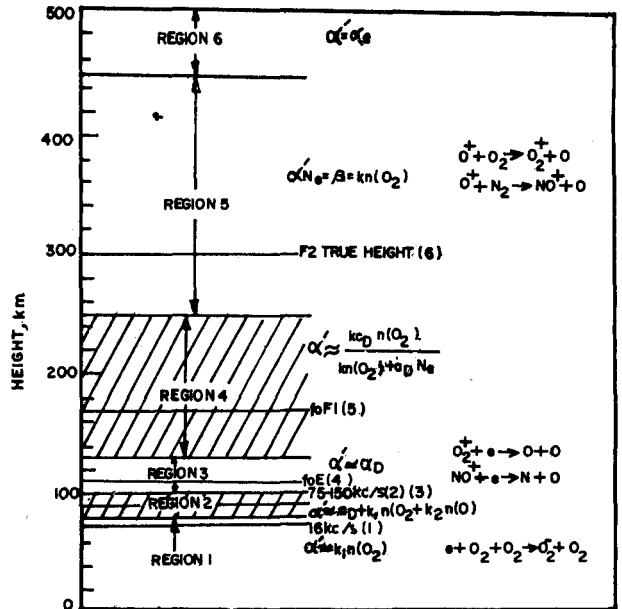


Fig. 5—Classification of regions in the ionosphere on the basis of dissipated processes (after Mitra)

go from regions dominated by negative ions ($\lambda\alpha_i$ term) to a combination of dissociative recombination and negative ion processes ($\alpha_D + \lambda\alpha_i$), to regions controlled entirely by dissociative recombination (90 to 150 km: α_D terms), then to a transition region where atomic and molecular ions are nearly equal, and finally to a region of atomic ions where atom-ion interchange converts O^+ ions to O_2^+ and NO^+ ions followed by dissociative recombination. The single expression that will cover the entire region from 60 to 600 km, was given as

$$\alpha = \alpha_D + \lambda\alpha_i + \frac{k\alpha_D[YZ]}{K[YZ]^+ \alpha_D N_e}$$

← — — — — — → ← — — — — — →
Lower Iono- F1 and F2 regions
sphere

or on the assumption that negative ions are formed by attachment to atomic and molecular oxygen, by:

$$\alpha = \alpha_D + k_1[O_2] + k_2[O] + \frac{k\alpha_D[YZ]}{k[YZ]^+ \alpha_D N_e}$$

He then stated that α over the entire ionosphere is completely specified if experimental data are used to give estimates for k_1 , k_2 , k , α_D . This he did by using Cambridge VLF observations (yielding k_1), Penn State observations on 75 and 150 kHz (yielding k_2), f_oE observations from Washington (yielding α_D) and true height profiles (yielding k). With these he derived the following expression.

$$\alpha' = 5 \times 10^{21} [\text{O}_2] + 3 \times 10^{-20} [\text{O}] + \frac{2 \times 10^{-19} [\text{O}_2]}{2 \times 10^{-11} [\text{O}_2] + 10^{-8} N_e} + 1 \times 10^{-12} \text{ cm}^3/\text{s}$$

In the F region this is reduced to an attachment-type coefficient given by:

$$\beta = 2 \times 10^{-11} [\text{O}_2] \text{ cm}^3 \text{ s}^{-1}$$

3 Ion Chemistry: IGY to 1970 (Phase II)

The IGY saw the emergence of a new area: ionospheric chemistry. The starting point was some very surprising results about ion composition in the ionosphere, as measurements began to become available from RF mass spectrometers flown in rockets and satellites. The unexpected dominance of NO^+ ions over much of the ionosphere where the initially produced ions are O_2^+ , N_2^+ and O showed the critical role played by ion chemistry. This prompted laboratory measurements of relevant reaction rates in a number of institutions and ion chemical modelling starting from reference neutral models. In the latter area two Indian groups were particularly active: that at NPL under AP Mitra and at Allahabad University under SN Ghosh.

Ion composition measurements with rockets such as those by Johnson and his colleagues in the USA covered heights up to 250 km. Above these heights, satellite-borne mass spectrometers were used: the Russian measurements with Sputnik III covered altitudes from 220 to 980 km in the latitude range 27° to 65°N during daytime. From both the USSR and US observations the following conclusions were made:

(i) The predominant positive ions were: O^+ , NO^+ and O_2^+ .

(ii) In the E-region (100-150 km), NO^+ was the predominant positive ion (although neutral nitric oxide is only a trace constituent) with an apparent diurnal-effect, $[\text{NO}^+]/[\text{O}_2^+]$ being larger during the day.

(iii) Above 200 km the predominant ion was O^+ ; above 250 km, all other ions become minor constituents.

(iv) As one went up from 100 to 200 km, the order of relative abundance of positive ions changed from (O_2^+ , NO^+) at 100 km to (NO^+ , O_2^+ , O^+) at 150 km and finally to (O^+ , NO^+ , O_2^+) at 200 km. O_2^+ and O^+ ions were roughly equal at heights 165-190 km. The pioneering set of observations on ion composition obtained by Johnson and his colleagues at NRL, USA, which became the starting point of ion chemistry, are shown in Fig. 6.

The surprising dominance of NO^+ ions and the virtual absence of N_2^+ ions were attributed to the ease with which the initially produced ions O_2^+ , N_2^+ , O^+ get converted to NO^+ through processes such as:

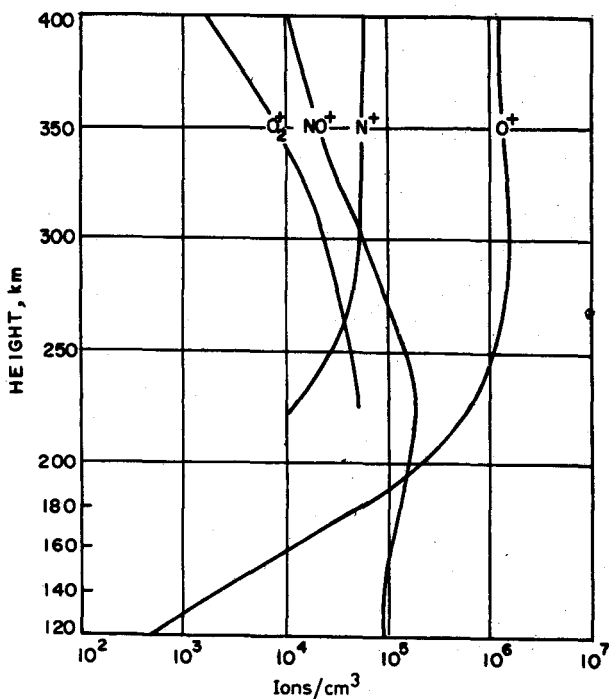
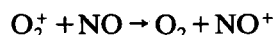
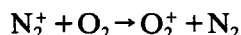
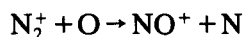
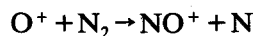
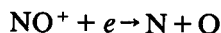


Fig. 6—Representative values of ions in the ionosphere measured during the IGY



The resulting NO^+ ions are destroyed through dissociative recombination:

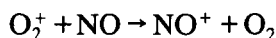


The ratio $[\text{NO}^+]/[\text{O}^+]$ was then expected to follow the equation.

$$\frac{[\text{NO}^+]}{[\text{O}^+]} = \frac{K_1[\text{N}_2]}{\alpha_D N_e}$$

The Indian workers (Mitra¹⁹) examined the observed changes $[\text{NO}^+]/[\text{O}^+]$ with height with varying values of K_1/α_D and found that a close correspondence exists for $K_1/\alpha_D = 1 \times 10^{-14}$, indicating a value of $5 \times 10^{-8} \text{ cm}^3/\text{s}$ for $\alpha_D(\text{NO}^+)$, then considered reasonable. An important result reported by Schmeltekopf²⁰ was that in the presence of internally excited N_2 the rate was much faster.

An important question concerned the role played by



which can become important if NO concentration exceeds 10^7 cm^{-3} . It was pointed out by Monro and Bo-

whill²¹ that the ratio $[\text{NO}^+]/[\text{O}_2^+]$ can provide a sensitive index of NO through the equation:

$$\frac{q(\text{NO}^+) [\text{O}_2^+]}{q(\text{O}_2^+) [\text{NO}^+]} \frac{\alpha_D(\text{NO}^+)}{\alpha_D(\text{O}_2^+)} \sim 1.8$$

where the q 's are the effective production rates for the ions, including both photoionization and two-body ionic reactions. For the typical ratio of 0.5 for $[\text{O}_2^+]/[\text{NO}^+]$ Monro and Bowhill found that the left hand side was too low by a factor of 7. There was thus an overabundance of O_2^+ and consequently the reaction involving NO was believed to be necessary to allow an increase in NO^+ abundance at the expense of O_2^+ . This exercise yielded an NO concentration of $2 \times 10^7 \text{ cm}^{-3}$ at 110 km. Another significant point was the observation of a decreasing trend in $[\text{O}_2^+]/[\text{NO}^+]$ with solar activity first pointed out by Mitra and Mitra²². At heights below 170 km, O_2^+ ions were greatly depleted during high solar activity while NO^+ ions were increased. This implied an increase in NO concentration during high solar activity: estimated to change from $3 \times 10^6 \text{ cm}^{-3}$ to $2.2 \times 10^7 \text{ cm}^{-3}$ (almost a factor of 10).

An important F region anomaly that was repeatedly discussed concerned the fact that the effective loss rate given by $\beta = k_1[\text{O}_2] + k_2[\text{N}_2]$ showed an order of magnitude discrepancy between the then available values of k_1 and k_2 and the value required to maintain the nocturnal F region ionization. Agreement with ionospheric observations required an inverse temperature dependence of the coefficients. Although a $T^{-1/2}$ dependence had then been observed for k_1 (which by itself was not sufficient), k_2 had been found to increase in the presence of the vibrationally excited N_2 . This had the effect of increasing the loss rate and thus increasing the anomaly. The distribution of O^+ , in consequence, assumes a simple form in the F region given by:

$$[\text{O}^+] = q(\text{O}) \beta$$

where β being dependent on the concentrations of O_2 and N_2 will vary with solar activity by a larger amount than $q(\text{O})$.

It was clear that the most critical component in the entire system was the distribution of neutral nitric oxide. The ultraviolet dayglow due to NO bands in the region 2000-3000 Å was observed by Barth and later by Pearce²³ and Meira²⁴. NO measurements were made in a number of ways and in number of places. Measurements were of the following types:

(a) rocket-borne measurements which, in most cases, used gamma band photometers (as in Barth-Pearce-Meira arrangements) or later in the modified photometer arrangement of Tohmatsu and Iwagami²⁵

(b) rocket-borne measurements in which a blunt probe detects changes in conductivity produced by Lyman- α radiation obtained from a flushing microwave discharge in hydrogen behind a lithium fluoride window (Pontano and Hale²⁶)

(c) satellite measurements of (1, 0) gamma band emission, relevant heights being 65-105 km

(d) indirect measurements in which use was made of the positive ion composition and, in particular, concentrations of NO^+ , O_2^+ and $\text{H}^+(\text{H}_2\text{O})_n$.

Rocket-borne measurements of type (a) were made in different latitude zones, viz. (i) high and auroral latitudes (Witt *et al.* and Tohmatsu and Iwagami²⁵), (ii) midlatitudes (Wallops Island by Barth, Pearce²³ and Meira²⁴; New Mexico by Baker *et al.*) and (iii) equatorial latitude (Thumba by Tohmatsu and Iwagami²⁵). These results are given in Fig. 7.

Indian contributions were based primarily in the context of ionospheric constraints. It was soon clear especially from theoretical works such as those of Brasseur and Nicolet²⁷ and Strobel²⁸ that use of low eddy diffusion coefficients and inclusion of photodissociation of nitric oxide give a rapid decrease in NO concentration in the mesosphere to values significantly lower than those observed (in the extreme cases of low coefficient as much as by two orders of magnitude) and a distribution substantially different giving a minimum in NO concentration near 70 km in contrast to the observed minimum around 85 km. Under these circumstances the Indian group considered it desirable and even necessary to fall back upon ionospheric measurements, including some controlled experiments specifically undertaken for this purpose. To define acceptable ranges of NO concentration several approaches were made: use of information on the level of ionization reversal with solar activity (Mitra²⁹), the gradual loss of solar control in the diurnal variation of electron density at levels below 70 km (Mitra³⁰) and the magnitude and changes in the ratio of two molecular ions $[\text{NO}^+]/[\text{O}_2]$ (Mitra and Rowe³¹; Narcissi *et al.*³²).

Satellite measurements were from over 4 satellites. These measurements were available over wide range of latitudes and over an extended period of time. Measurements also covered both day and night conditions. An important conclusion was that high latitude values were on the average four times larger than low and midlatitude values.

A specially interesting approach was a series of controlled experiments using the high power wave interaction facility at Pennsylvania State University to monitor, with high time and height resolution, changes in mesospheric ionization during solar flares along with simultaneous satellite-borne observations

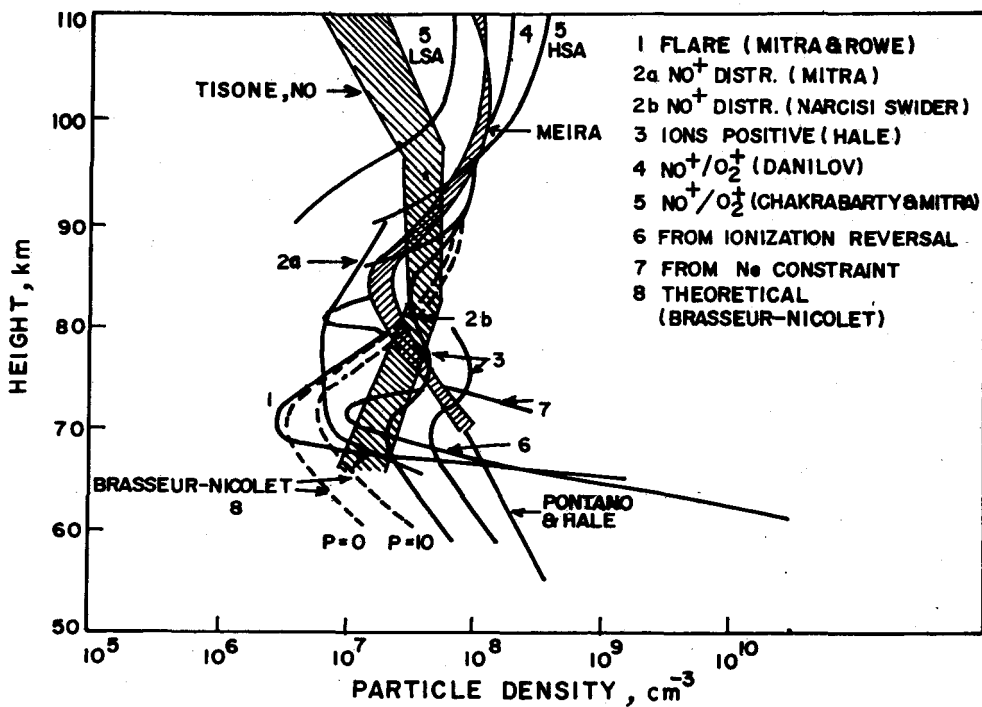


Fig. 7—Ionospheric estimates of nitric oxide in the mesosphere and lower thermosphere

on the time changes in X-ray flux and its spectral structure. These various ionospheric estimates are also given in Fig. 7.

Both flares and solar cycle reversals in N_e showed very low NO values around 70 km. However, the diurnal variation of NO^+ ions and the N_e constraints as well as gamma band measurements indicated a minimum around 80 km.

Much of the efforts, especially from the Indian groups, centred on the D region. The first major result is that much evidence has accumulated to indicate that during solar flares and PACs the effective recombination coefficients in the D region are drastically reduced. During solar eclipses, on the other hand, the coefficients increased to near-night values. Deshpande and Mitra³³ studied most extensively the changes in α during solar flares (using quantitative comparisons of SCNAs and accompanying solar flares) for a total of 50 large solar flare events and found that the decrease was in proportion to the size of X-ray flare. Examples for 70 and 80 km are shown in Fig. 8: the decreases were found to be astonishingly large at some heights by as much as two orders of magnitude.

The second major result seen was the drastic decrease, for both day and night (but particularly drastic at night), of water cluster ions relative to molecular ions in the D region during PACs. Much of these observational results came from the work of Narcissi *et al.*³² with rocket measurements of positive and nega-

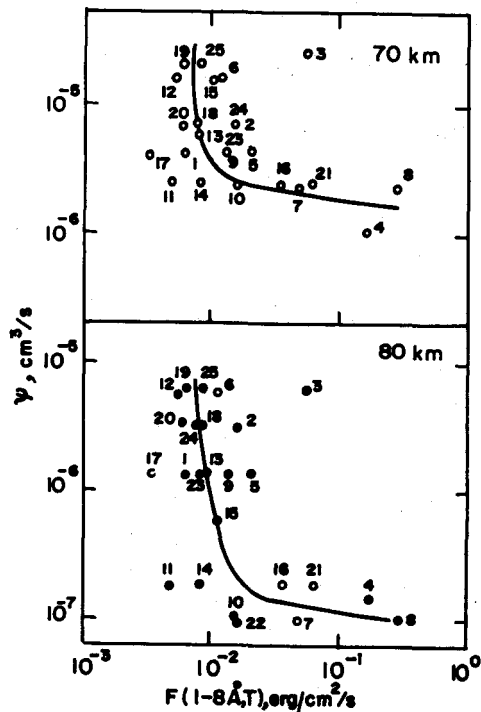


Fig. 8—Reduction of the loss rate at 70 and 80 km during solar flares as a function of the X-ray flux at 1-8 Å unit

tive ion composition during PCA day and PCA night (3 Nov. 1969). The cluster disappearance level descended from its quiet day height of about 82 km to at least 73 km and perhaps lower. There was a similar lowering of the night cluster disappearance level from

its normal value of about 87 to about 77 km. The third major point of the D region was its complexity and sharp variations in composition and concentration of negative ions within tens of kilometres.

To explain the D region in its entire complexity both during quiet times as well as conditions of PCAs, solar flares and eclipses, complex ion schemes were formulated by a number of workers, notably by Reid³⁴, Thomas³⁵, Mitra³⁶ and Rowe *et al.*³⁷ But since many of the steps in the reaction sequences were inadequately known there was considerable danger in using complex reaction schemes which involve steps of a purely hypothetical nature. To obviate this, Mitra and Rowe³⁸ introduced a simplified 6-ion model of D region ion chemistry which takes the form shown in Fig. 9. It offered certain advantages over complex schemes in constructing the D region profiles under quiet and disturbed conditions. First, it eliminated some of the uncertain and hypothetical (and for electron density unnecessary) steps in the reaction sequence.

Secondly, as the parameters involved are fewer and are related explicitly to specific measurements on electron density, positive ion density and positive and negative ion composition, a semi-empirical approach was possible. Thirdly any part of the scheme could be expanded as and when the steps were considered reliable.

The critical parameter was *B*, the effective rate of conversion of NO⁺ and hydrate ions. The requirement on *B* so that water clusters for a concentration of 50% of the total positive ions, was found to be:

$$B = 10^{-2} \text{ s}^{-1}$$

The simple scheme gave an unusually faithful representation of not only the daytime conditions but also conditions during solar flares, PCAs and solar eclipses. During the flare as well as during PCAs there is

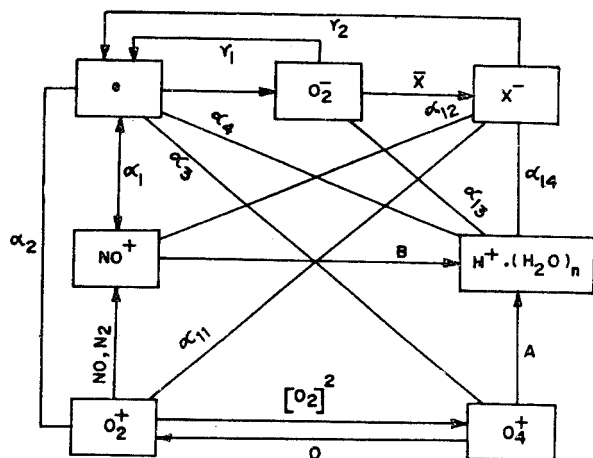


Fig. 9—Six Ion Scheme of Mitra and Rowe for mesospheric positive and negative ions

a sudden large supply of O₂⁺ ions produced both through direct photoionization of O₂ and through charge transfer from N₂⁺. There is now a sudden shift of clustering channel from NO⁺ → clusters to the channel O₂⁺ → O₄⁺ and from O₄⁺ partly to hydrates and partly to O₂⁺ through back reaction involving atomic oxygen. Thus all the ions are lost for clustering and go back into O₂⁺ and NO⁺. The resulting decrease as *q*(O₂) is increasing is shown in Fig. 10 along with observational results.

4 The Ozone Problem: 1970-To Date (Phase III)

The ozone problem is a recent one—hardly two decades old. It was in 1971 that Crutzen and Johnson first pointed out the possible hazards of the large scale injection of NO from supersonic aircrafts to stratospheric ozone. The ozone controversy played an important role in the political debate on SSTs in the USA in early 1971 and eventually resulted in the cancellation of SST development in the USA. The second thrust came when Rowland pointed out that C1X coming from the propellants used in aerosol sprays can also attack ozone. In quick succession a number of other manmade ozone-attacking sources were brought forward. The manmade and natural chemicals of interest include NO_x from subsonic and supersonic aircraft, N₂O from agricultural practices, chlor-

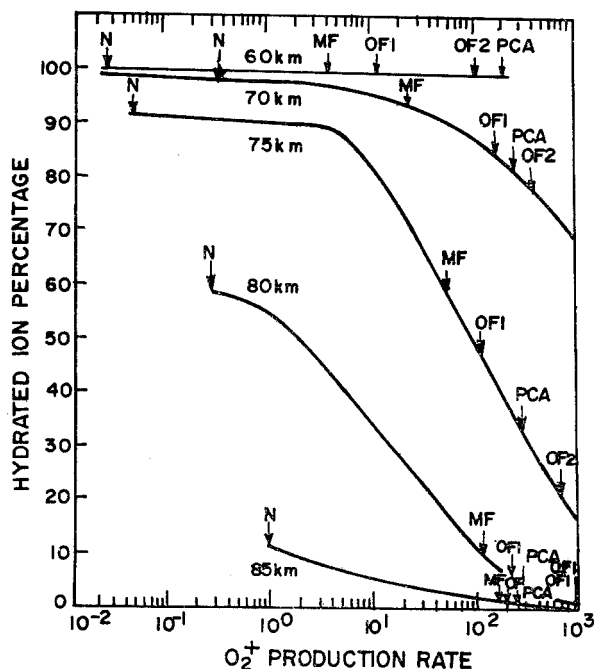
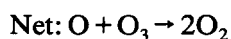
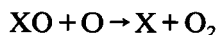
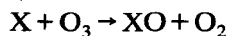


Fig. 10—Theoretical calculation showing the decrease of hydrated ion percentage with the O₂⁺ production rate during solar flares of different magnitudes and polar cap absorption events (The different curves represent different heights. The symbols have the following meanings: N represents normal condition, MF—Moderate Flare, OF—Outstanding Flare, PCA—Polar Cap Absorption events.)

ofluorocarbons used as aerosol propellants, from blowing agents and refrigerants, brominated compounds used as fire retardants, CO and CO₂ from combustion processes and CH₄ from a variety of sources including natural and agricultural wet lands, tundra, biomass burning and enteric fermentation in ruminants.

The catalytic cycles involved in the destruction of ozone in homogeneous gaseous reactions of active free radical species in the HO, NO, ClO and BrO families are given by:



where the catalyt X = H, OH, NO, Cl and Br.

In dealing with ozone photochemistry, efforts were concentrated on: (a) detailed descriptions of the basic chemical and photochemical processes occurring in the atmosphere and controlling ozone and other trace gas budgets, (b) sources measurement and estimation of sources distribution and trends of critical tropospheric and stratospheric trace gases, (c) dynamical processes, (d) 1-D, 2-D and 3-D assessment models, (e) model calculations giving estimates of the response of atmospheric composition to a variety of

potential perturbations and (f) effects of the trace gases on climate.

Indian interest in ozone is several decades old. Over the years four principal types of measurements were introduced: surface, Dobson, balloon-borne chemical ozonesondes and rocket payloads. The stations and types of measurements are listed in Table 2. Rocket measurements are more recent. The principal series of rocket campaigns on ozone were during the Solar Eclipse Campaign of Feb. 1980 (in which groups from the Physical Research Laboratory at Ahmedabad and the National Physical Laboratory at Delhi participated), participation by the PRL group in the International Wallops Island Intercomparison Campaign and, March 83 Campaign of Ozone Intercomparison involving Indian and Soviet scientists from Thumba.

A somewhat unique type of measurement introduced in India several years back was direct measurement of absolute fluxes at the ground with three photometers working at 280, 290 and 310 nm. These are photometers directly measuring the changes in UV-B dosage instead of indirect estimates from determinations of ozone by other means.

Of the critical minor species which are important in the ozone chemistry, only very few have been measured in India. For water vapour most measurements are for the lower troposphere and radiosonde is the

Table 2—Types of Ozone Measurements

Type or mode of measurement	Place and other details	
*Balloons	Poona, New Delhi, Trivandrum	Fortnightly
	From 1971 onwards	
	Intercomparison with six other countries in 1970 at Hohenpeissenberg	
	Deviations: + 15% in Troposphere - 5% in Stratosphere	
	Several improvements since	
*Dobson spectrophotometer	Srinagar, New Delhi, Varanasi, Mt. Abu, Poona, Kodaikanal	Daily during daytime, at least 5 observations Umkehr whenever possible
	*Intercomparison with National Standard Spectrophotometer at New Delhi—latter standardised with world standard at international intercomparison in Boulder 1977	
	Available from 1960 onwards	
	*O.T Delhi data being coordinated with US satellite over-passes	
*Surface ozone	Poona, Trivandrum, New Delhi, Kodaikanal, Nagpur	
*Ground UV-B	Delhi - NPL 280 10, 290 10, 300 10 nm	About one year
*Rockets	Several flights from Thumba 4 Flights from Thumba during Eclipse Intercomparison in Wallops Islands, 1979	

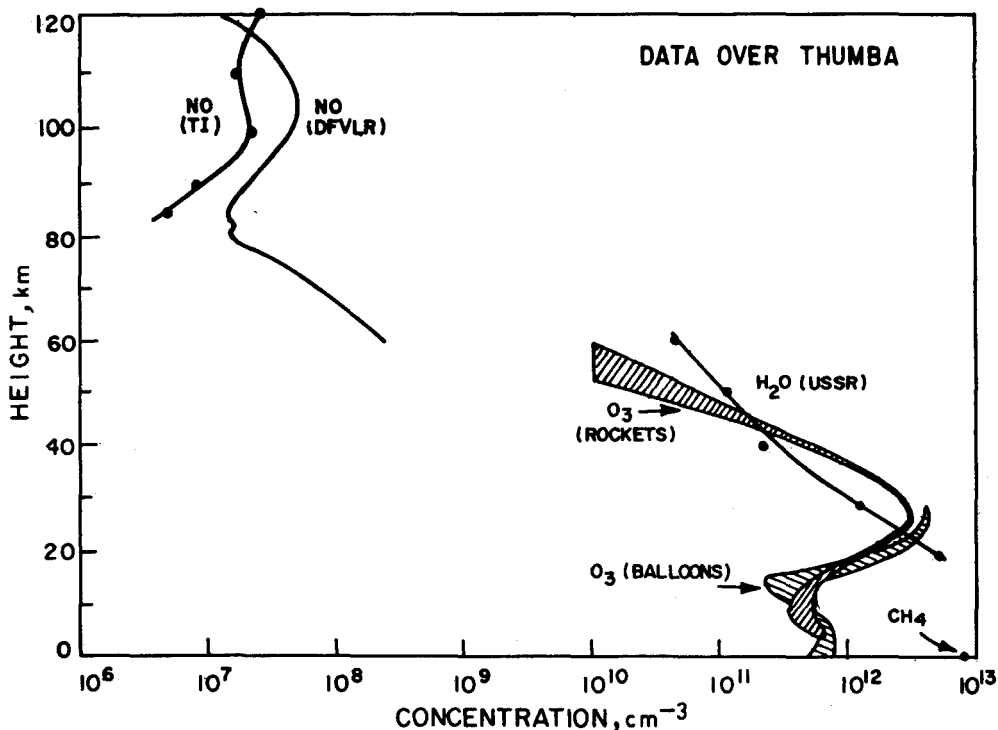


Fig. 11—Observations of minor species in India, all obtained over Thumba (The two nitric oxide profiles are those of Tohmatsu and Iwagami and of the DFVLR group. Ozone measurements given are those taken during the Indo-USSR Intercomparison Measurements in March 1983 and range of values are indicated through shades. Methane measurement is at ground with a gas chromatograph by the NPL at IARI campus. The water vapour measurements are those carried out by Soviet scientists over Thumba.)

Table 3—Important Nitrogen Oxygen Reactions Considered by Mitra³⁹

Reaction	Rate
$N + O \rightarrow NO + O$	$(1.4 \pm 0.2) \times 10^{-11} e^{-3600 \pm 200/T}$
$N + O + M \rightarrow NO + M$	$1.1 \times 10^{-32} (T/300)$
$N + O \rightarrow NO + h\nu$	2×10^{-17}
$N + NO \rightarrow N_2 + O$	2.2×10^{-11}
$N + O_2(^1\Delta_g) \rightarrow NO + O$	$\geq 4 \times 10^{-14}$
$NO + O_3 \rightarrow NO_2 + O_2$	$9.5 \times 10^{-13} e^{-1300 \pm 100/T}$
$NO_2 + h\nu \rightarrow NO + O$	5×10^{-3}
$O + NO_2 \rightarrow NO + O_2 + 46 \text{ kcal}$	$(2.8 \pm 0.9) \times 10^{-11} e^{-550 \pm 100/T}$

principal source of measurement. In a more limited way, microwave radiometry (with radiometers located at the ground as in the NPL and more recently in Calcutta University and in the satellite as in Bhaskara I and II) is available. For stratospheric heights values available are those determined by Soviet scientists over Thumba with M-100 rockets.

NO estimates are available only for tropospheric heights through a joint NPL-Tokyo University with rocketborne γ -band photometers over Thumba and more recently through a joint experiment between PRL and West Germany. Indian workers' values for minor species (principally over Trivandurm) are shown in Fig. 11.

The possible role of NO in ozone chemistry was pointed out by Indian workers as early as 1969

(Mitra³⁹). The important nitrogen oxygen reactions considered by him are given in Table 3.

Since then there has been virtually no work relating to ozone chemistry by Indian workers, excepting recently by Mitra in which an attempt was made to estimate the history of NO_x input during the last three decades. For this effort he used the *Catalogue of Solar Particle Events 1955-69* given by Svestka and Simon⁴⁰ and Smerd-Shea Index⁴¹. A total of 173 significant events for the period 1955-73 were used. The parameter used was the quantity $F = (\sum A(dB) \times \text{duration})$. This was converted into NO_x injection value using August 1972 case for which NO_x input was estimated to be 30×10 molecules. The estimated time history of the NO_x input compared to inputs by nuclear explosions, individual large flare events such

as those of July 1959 and August 1972 as well as the contribution of galactic cosmic rays are shown in Fig. 12.

However, a good bit of work has been done on the analysis of ozone profiles both from balloon mea-

surements as well as from rocket measurements. A Reference Ozonosphere over India has been produced by Kundu⁴² using primarily data over Trivandrum (8°N), Poona (18°N) and Delhi (28°N) for the period 1960-76 (Fig. 13). Rocket observations during the Solar Eclipse of Feb. 1980 as well as an earlier Indo-USSR collaborative programme made during 1979-80 and the series of flights in 1980-81 by PRL have been examined by Subbaraya⁴³. Some of these estimates are shown in the same diagram.

A new technique for realtime monitoring of ozone profile is under development at the NPL with a Laser Heterodyning System. The capability of the technique in retrieving ozone profiles is shown in Fig. 13 (S.L. Jain, private communication).

The direct UV-B flux measurements at NPL by Srivastava have provided some information on erythmal dose for several stations in India. There has also been some attempt to see the occurrence statistics of melanoma and non-melanoma cases on skin in Indian patients compared to other countries. The Indian data were taken from Bombay Cancer Registry. The occurrence frequency (per hundred thousand) is apparently less frequent with Indian patients than for North European and North American people. This is also the case for Indians in Singapore.

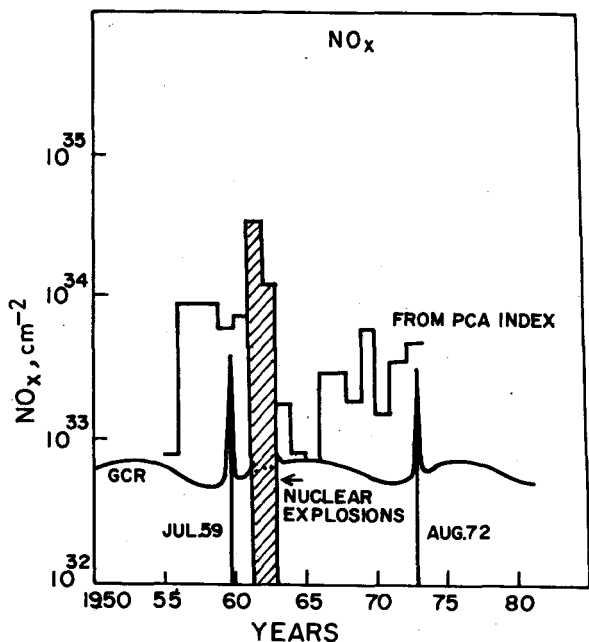


Fig. 12—A history of NO_x variation over the last three decades calculated by Mitra showing the role of polar cap absorption events

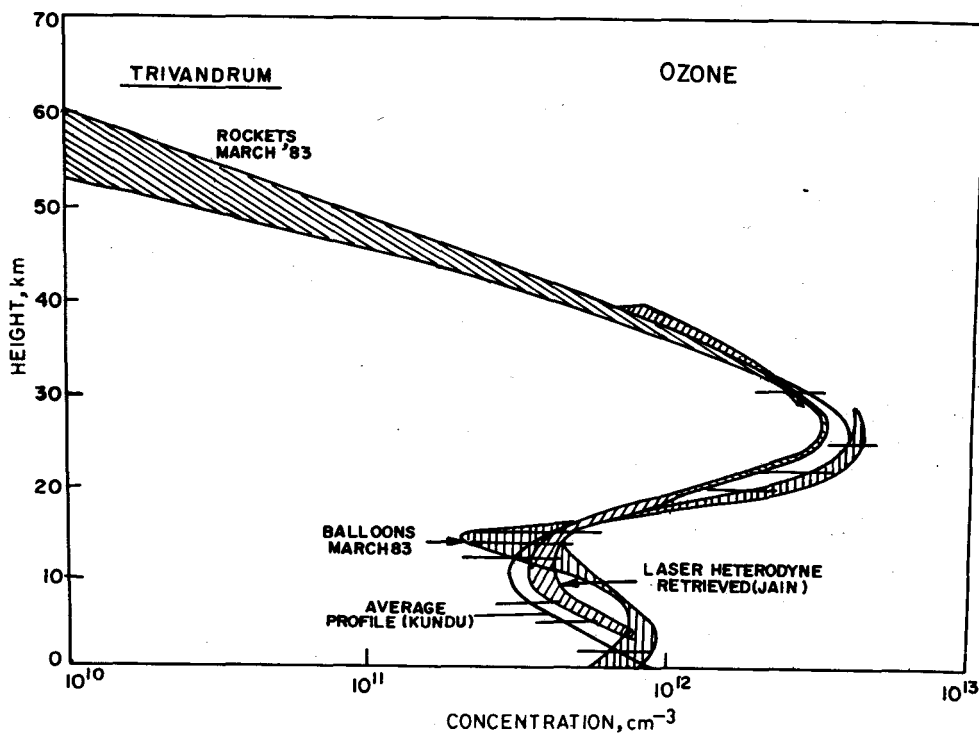


Fig. 13—Representative ozone profiles over India [The profile marked 'Average Profile' is that of Kundu (with ranges shown by bars); the balloon and rocket values during the Intercomparison. Experiment in March 1983 and the retrieved profile are by S.L. Jain with the laser heterodyne system.]

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