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THE NITROGEN OXIDES CONTROVERSY

Harold S. Johnston

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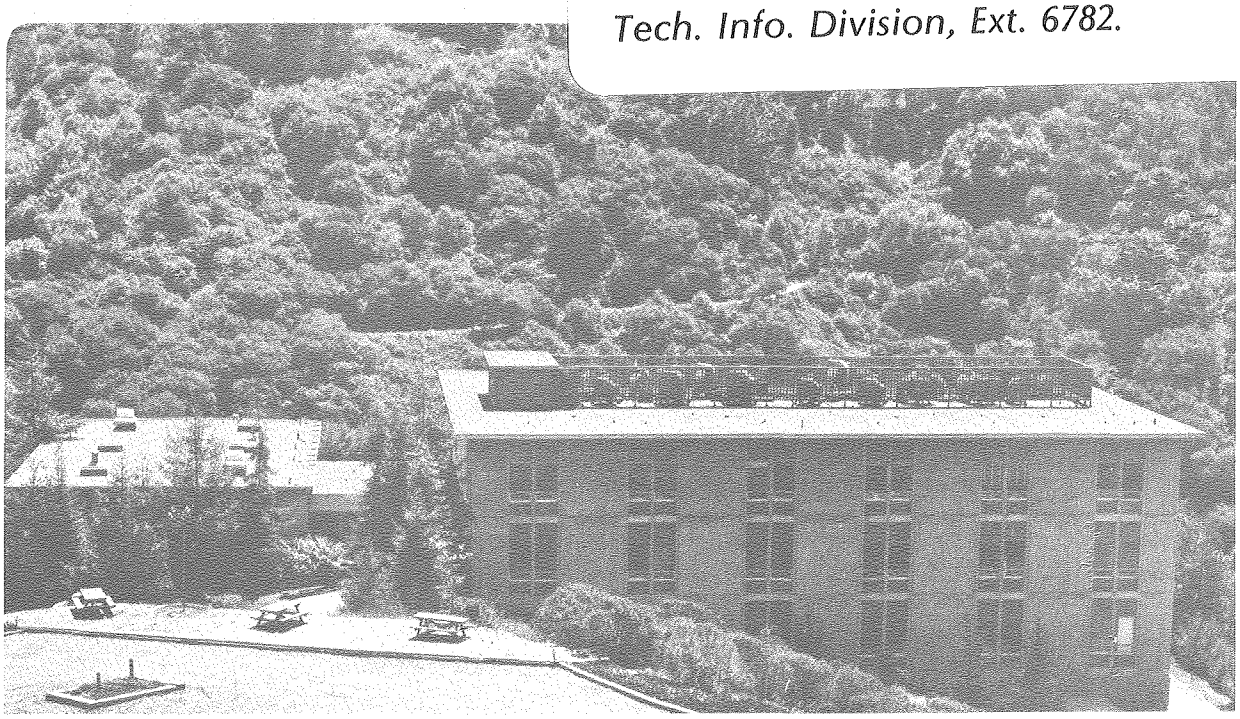

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The Nitrogen Oxides Controversy

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The SST Controversy Ten Years Later: A Case Study in the Use of Science for Decision Making

Organized by S. Fred Singer and H. I. Schiff

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Abstract

With ten-year hindsight, the scientific considerations that entered discussions of possible changes of stratospheric ozone by large fleets of US-type SSTs are seen to be logical and constructive. Since 1961, it has been realized that the photochemistry of the natural ozone balance cannot be explained in terms of pure oxygen species (O_x = O, O_2, O_3), but that "something else" in the stratosphere destroys most of the ozone formed at and below the altitude of its maximum mixing ratio. When (1965-70) this natural ozone destruction was thought to be caused by a few ppm of water, it was pointed out that the predicted 10 percent increase in stratospheric water by SSTs was a matter of concern. When (1970-71) it was found that a few ppb of nitrogen oxides (NO_x = NO, NO_2) probably are the major cause of natural ozone destruction, then it was pointed out that the predicted doubling of stratospheric NO_x by SSTs was a matter of concern. These were valid statements of the need for an environmental impact assessment. This area of science was primitive in 1970, but by 1981 it has a large body of laboratory and atmospheric measurements and elaborate matehmatical models. During this evolution, the models have changed their NO_x-SST predictions from an ozone-column decrease (1971-1976), to an ozone-column increase (1977-early 1980), and back again to an ozone-column decrease (October 1980-). Although these changes in prediction may appear to be a "comedy of errors," what we really have is the history of a dedicated group of scientists working out the solution to a complex problem. I estimate that within another 10 years, scientists of the stratosphere will be able to make firm predictions about the effect of nitrogn oxides on stratospheric ozone.

I. Introduction

The subtitle of this symposium is "A case history in the use of science for decision making." To carry out this study of a case history, it is important to examine the nature of the science being used and to note its degree of maturity 10 years ago and today. This sub-field of science might be called "stratospheric photochemistry and dynamics," which cuts across several scientific disciplines. This field is concerned with detailed aspects of atmospheric motions, stratospheric composition, solar and terrestrial radiation, and photochemistry. These subjects are studied by the methods of atmospheric observations, laboratory measurments, theoretical interpretations, and mathematical models. From the start we should recognize that all four of these methods are capable of contributing to the advancement of the science, but also each of them is subject to error and mistakes.

I want to look at the history of this subject from two points of view: The first point of view concerns the important variables involved in the balance between formation and destruction of stratospheric ozone. This problem is tightly coupled to observations, involves a minimum use of mathematical models, and in the early stages of the subject was instrumental in identifying supersonic transports as a potential cause of ozone reduction. The second point of view is that of mathematical models of the atmosphere. Within their limited frame of reference these models predict the effect of various perturbations of the atmosphere, such as supersonic aircraft.

This subject has been reviewed at various stages in the past, for example, Grobecker et al. (1974), Johnston (1975), National Research

Council (1975), Broderick (1977), Logan *et al*. (1978), NASA (1979) and Luther (1979).

II. The Natural Balance of Stratospheric Ozone

Stratospheric ozone (O_3) is produced by breaking apart molecular oxygen (O_2) by far ultraviolet solar radiation ($h\nu$)

$$O_2 + h\nu \ (\lambda < 242 \text{ nm}) \quad O + O \tag{1}$$

$$(O + O_2 \xrightarrow{M} O_3) \text{ Twice} \tag{2}$$

$$\text{net:} \quad 3\ O_2 + h\nu \rightarrow 2\ O_3$$

The photochemical break-down of ozone to $O_2 + O$ usually does not lead to ozone destruction, because with rare exception it is followed by reformation of ozone by reaction (2). Occasionally, ozone photolysis is followed by ozone destruction through the chemical steps

$$O_3 + h\nu \text{ (visible, UV)} \rightarrow O_2 + O \tag{3}$$

$$O + O_3 \rightarrow O_2 + O_2 \tag{4}$$

$$\text{net:} \quad 2\ O_3 + h\nu \rightarrow 3\ O_2$$

Chapman (1930) proposed that the photochemical reactions, (1), (2), (3), and (4), were responsible for the natural balance between ozone formation and destruction in the stratosphere.

To test the adequacy of this mechanism, Chapman and his followers in this field between 1930 and the early 1950's were forced to make assumptions about the distribution of far ultraviolet radiation above the atmosphere, and they were forced to use indirect measurements of the rate coefficients for reactions (2) and (4). Typically they assumed that radiation from the sun corresponded to the Planck radiation law for 6000 K. The Planck function for 6000 K gave a reasonably good fit to visible and near ultraviolet radiation, which reaches the earth's

surface; and it was assumed to be valid at shorter, more energetic wave lengths. Around 1950, the Chapman mechanism involving the O_x family of species, O, O_2, O_3, appeared to explain the natural ozone balance (Mitra, 1952).

During the 1950's rockets were sent high above the stratosphere, and these flights were used to measure solar radiation above the atmosphere. It was found that the distribution of solar ultraviolet radiation above the atmosphere did not follow the Planck function for 6000 K (Johnson et al., 1954, Detwiller et al., 1961). During the 1950's several new laboratory methods (for example, shock tubes, flash photolysis, and fast flow systems) were developed that permitted direct observation of active species such as atomic oxygen and that gave new values for the rate coefficients of atmospheric reactions (compare the review by Kaufman, 1964). Dütsch (1961) pointed out that the theory based on reactions (1) to (4) indicated far more ozone than that observed. Hunt (1966a) wrote a paper entitled "The Need for a Modified Photochemical Theory of the Ozonosphere," in which he demonstrated that the calculated ozone profile was greater than that observed at all altitudes, and the vertical ozone column exceeded that observed by a factor of 3 to 4. It appeared that "something else" besides O_x species was very important in destroying ozone in the stratosphere.

The water reactions - In a subsequent paper, Hunt (1966b) tested Hampson's (1964) suggestion that ozone was destroyed by catalytic cycles based on free radicals derived from water, H, HO, and HOO, which are collectively referred to as HO_x. One such catalytic cycle is

$$HO + O_3 \rightarrow HOO + O_2 \quad (5)$$

$$HOO + O_3 \rightarrow HO + O_2 + O_2 \quad (6)$$

$$\text{net:} \quad 2\ O_3 \rightarrow 3\ O_2$$

Hunt concluded that this mechanism would give agreement with ozone observations <u>if</u> the rate coefficients for reactions (5) and (6) were

$$k_5 = 5 \times 10^{-13}\ cm^3\ s^{-1}$$

$$k_6 = 1 \times 10^{-14}\ cm^3\ s^{-1}$$

During the period 1966-71, Hunt's postulate became the working model for the stratospheric ozone balance even though these rate coefficients had not been measured. Langley and McGrath (1971) reported laboratory measurements that indicated k_5 to be less than 1×10^{-16} $cm^3\ s^{-1}$, that is, 5000 fold less than that required for Hampson and Hunt's mechanism. This result suddenly demolished Hunt's model, but later experiments (1973-79) showed Langley and McGrath's result to be quite wrong. The apparent value of the rate coefficient k_5 as a function of time between 1965 and 1980 is shown by Fig. 1. Recent experiments (1973-79) show that both k_5 and k_6 are about a factor of 10 lower than required by Hunt (Baulch <u>et al</u>., 1980; NASA, 1979).

<u>The NO_x mechanism</u> — From a balloon, Murcray and co-workers (1968) observed nitric acid (HNO_3) and probably nitrogen dioxide (NO_2) at a few parts per billion in the lower to middle stratosphere. In reflecting on these observations, Crutzen (1970) recognized that the oxides of nitrogen are capable of destroying ozone in a catalytic cycle

$$\begin{array}{ll} & NO + O_3 \rightarrow NO_2 + O_2 \\ & NO_2 + O \rightarrow NO + O_2 \\ \hline \text{net:} & O_3 + O \rightarrow O_2 + O_2 \end{array} \qquad (7)$$

The net result is ozone loss as in reaction (4), catalyzed by NO and NO_2. In the context of pure science, Crutzen postulated that NO_x (that is, NO and NO_2) could be responsible for maintaining the natural ozone balance, _if_ NO_x is present at about 10 parts per billion in the stratosphere.

During the period 1972-1980, many observations have been made of stratospheric NO, NO_2, and HNO_3. Noxon _et al_. (1979) and Noxon (1979, 1980) observed the vertical column of NO_2 at many latitudes and seasons. Several balloon flights have given the NO_x vertical profiles in the stratosphere (NASA, 1979). Noxon's observed NO_2 profiles have been translated by Solomon _et al_. (1980) into a global, three-dimensional distribution of NO_2; and using Noxon's (1980) recalibration of his method, it was found that NO_x destroys ozone in the "ozone formation region" between 15 and 45 km at about 60 percent of the rate of ozone production over the same range. These observations (Noxon, 1979, 1980) and calculations (Solomon _et al_., 1980) confirm Crutzen's (1970) hypothesis about the amount and distribution of NO_x in the stratosphere, in contrast to the disproof of the hypothesis by Chapman concerning solar radiation above the atmosphere and the hypothesis of Hunt about the values of two rate constants. Here we have the classic operation of the scientific method; hypotheses are made, tested, and replaced until the correct statement is found.

At present it appears that catalysis by NO_x is, by far, the dominant loss mechanism for ozone in the natural stratosphere. It also appears that O_x, HO_x, and chlorine-containing species each contribute significant direct destruction of ozone, and these species interact in important ways with the oxides of nitrogen. These interpretations about the natural ozone balance are strongly anchored to observations of trace species in the atmosphere, and they are almost independent of stratospheric models.

SSTs in context of our understanding of the natural ozone balance — During the period 1965-1971, it appeared that the HO_x free radicals derived from natural water were responsible for destroying about 80 percent of the ozone produced in the "ozone formation region" of the stratosphere, that is, below about 45 km, if two unmeasured rate coefficients had sufficiently large values. In the period 1969-1970, various analyses concluded that a large fleet of U.S.-type supersonic transports would be expected to increase stratospheric water vapor by about 10 percent on a global scale and by a larger percentage at mid-latitudes in the flight corridors of the northern hemisphere. The general proposition was that if natural water is the dominant cause of ozone destruction in the natural stratosphere, then increasing stratospheric water vapor by 10 percent or more is a matter of legitimate concern. This argument was a logical and constructive one, until Langley and McGrath's (1971) reported rate coefficient contradicted its foundation.

Meanwhile, Crutzen (1970) had found that the oxides of nitrogen could account for the natural ozone balance, if NO_x was present in the

stratosphere at more or less 10 parts per billion. At a meeting in Boulder, Colorado of the SST Environmental Research Panel of the U.S. Department of Commerce Technical Advisory Board, Park and London (1971) presented a reasonable natural distribution of stratospheric NO_x on the basis of observed NO_x in the mesosphere, observed NO_x in the troposphere, and with continuity through the stratosphere. They inferred an average stratospheric NO_x column that was five parts per billion, which was in reasonable agreement with Crutzen's expectations. Park and London also deduced the "maximum credible" distribution of NO_x from the exhausts gases of a large fleet of supersonic transports operating at 20 km altitude, and this input increased the stratospheric NO_x load to 27 parts per billion, which is an increase by more than a factor of five. This factor of five includes a large "corridor effect," and the indications were that on a global scale a large fleet of SST's would more or less double stratospheric NO_x.

In the years after the meeting of the SST Environmental Research Panel in Boulder, Colorado, March 1971, it is sometimes forgotten what the issues were at that time. The primary concern at that meeting was the effect of water vapor on ozone. Park and London added their discussion of nitrogen oxides as an afterthought to their paper on water vapor. McElroy (1971) explored the possibility that NO_x from SSTs might be transported into the D-region of the ionosphere, provide an additional source of ions, and possibily have an effect on radio propagation; one member of the Panel a year later cited this effect as the most serious issue so far as SST nitrogen oxides were concerned. The SCEP report (1970) said "... in stratospheric photochemistry ...

NO_x ... may be neglected." At that meeting, I proposed a formal motion to the SST Environmental Research Panel: "We recommend that the oxides of nitrogen be regarded as potentially an important variable in problems concerning stratospheric photochemistry." After a discussion and a vote, the SST Research Panel rejected this motion. These examples illustrate the primitive nature of our understanding of NO_x photochemistry in the stratosphere in 1971.

During 1971 and 1972 the following argument was stated on several occasions: If natural NO_x is the dominant cause of ozone destruction in the natural stratosphere, then more or less doubling stratospheric NO_x by supersonic transports is a matter of legitimate concern, and it may not be neglected. The proponents of the proposed U.S. supersonic transports, which to a large extent was the U.S. Government, were under obligation to assess the environmental impact of large increases in NO_x. This obligation has been recognized and is being met by the Climatic Impact Assessment Program (1971-1975), by the High Altitude Pollution Program, by NASA, and by other on-going programs.

III. Mathematical Models of the Atmosphere

Models typically employ computer programs, use simplified expressions for atmospheric motions, take laboratory measurements as input data, and take atmospheric observations as boundary values. These models calculate the species profiles in the natural atmosphere, and they calculate how these profiles change for assumed perturbations of the stratosphere. The ideal model would include the global atmosphere with motions in three dimensions, it would include a complete set of atmospheric species and photochemical reactions, and it would include all forms of solar and thermal radiation. Such a model is too complex for 1981 resources. It has been necessary for scientists working in this field to construct simplified models that explore certain aspects of the real world. Some models include three-dimensional motions and a small amount of chemistry (Mahlman *et al.*, 1980). Several models include only the global-average vertical component of motion but have extensive sets of chemical reactions (Chang and Duewer, 1979).

In particular, models have calculated natural ozone profiles and ozone profiles after the long-term operation of large fleets of supersonic transports. Some of the history of these calculations over the past 10 years will be reviewed.

SST's and the water reactions — During the period (1969-1971), when water vapor was regarded as the major source of natural ozone destruction, some model calculations were made of changes in the ozone column subject to large increases in water vapor from supersonic transports. The Boeing Research Laboratory gets the credit for

pioneering work in this field; Harrison (1970) of the Boeing Laboratory published a model calculation giving a 3.8 percent reduction of ozone by water from a large fleet of SSTs. Of course these predictions were made in the context of the knowledge of the time; and when it appeared that the HO_x-ozone rate coefficients were low, these model calculations were superseded.

SST's and NO_x reactions — The first model calculation of ozone reduction by SST-produced nitrogen oxides appears to have been made by Park and London (1971). They deduced an NO_x background that averaged five parts per billion, they concluded that the large fleets of SSTs proposed in 1971 might increase stratospheric NO_x by about a factor of five, and they calculated a 1.8 percent reduction of the ozone column.

It was at this point that I got into the field of stratospheric photochemistry. I would like to comment on my personal role in 1971 and again in 1974.

Park and London calculated only a 1.8 percent reduction in ozone for a large increase in stratospheric NO_x. I spotted the fact that, by mistake, they had used a value for a well-known rate coefficient that was too large by a factor of 10,000, and in that case, the oxides of nitrogen very powerfully produce ozone by the catalytic cycle

$$2\ NO + O_2 \rightarrow 2\ NO_2 \qquad (9)$$

$$\left(\begin{array}{l} NO_2 + h\nu \rightarrow NO + O \\ O + O_2 \xrightarrow{M} O_3 \end{array}\right) \text{twice} \qquad \begin{array}{l}(10)\\(2)\end{array}$$

$$\text{net: } 3\ O_2 + h\nu \rightarrow 2\ O_3$$

When I repeated Park and London's calculation with the correct value of k_9 and with Langley and McGrath's (1971) value of k_5, the model calculation gave a 49 percent reduction of ozone. (The details of this episode are given by Johnston, 1974.)

I went on to make other similar model calculations for a wide variety of assumed NO_x background profiles and for a wide variety of NO_x perturbations (Johnston, 1971a,b). In one series of cases, I showed that for a given background NO_x profile and for a given mass of NO_x perturbation, one could calculate ozone reductions anywhere between 3 percent and 50 percent depending on the distribution of the NO_x in the stratosphere, and all of these distributions appeared reasonable within the context of current discussions of atmospheric motions (Danielson, 1971). Although I, like Park and London, used an extremely simple model, it established — at least to my satisfaction — that the effect of added NO_x on ozone depended strongly on three features: (i) the natural NO_x background, (ii) the magnitude of the NO_x perturbation, and (iii) the distribution of the NO_x perturbation.

During 1971, at least two other authors made model calculations indicating that NO_x from large fleets of supersonic transports might significantly reduce stratospheric ozone (Westenberg, 1971; Crutzen, 1971).

In 1974 a co-worker and I (Johnston and Quitevis, 1975) pointed out another three-fold aspect of the effect of NO_x on ozone: (i) In photochemical smog in the lower troposphere, added NO_x produces ozone; (ii) in the middle and upper stratosphere, added NO_x reduces the local concentration of ozone, and (iii) therefore, there must be some altitude

at which these effects cross such that local ozone is unaffected by added NO_x. Model calculations were carried out including HO_x, NO_x, and methane reactions as they were understood to be at the time. The cross-over point between ozone production by the NO_x-methane smog reaction and ozone destruction by reactions (7) and (8) appeared to be about 13 km, Fig. 2. An airplane flying at some altitude would send some of its NO_x up into the region where NO_x destroys ozone and some of its NO_x down to the region where NO_x and methane produce ozone. The flight altitude of zero effect on the total ozone vertical column is not the same as the altitude of zero local effect. Even so, our simple calculation showed that the effect of aircraft on ozone also included this additional complication and that at some flight altitude the NO_x from an airplane should increase the ozone vertical column.

During the period 1972-1980, the atmospheric models have increased in physical, chemical, and mathematical sophistication. During this period, many photochemical reactions of stratospheric significance have been studied or reinvestigated in the laboratory; and in a number of cases, powerful, direct methods have been employed. A number of groups have carried out model studies of stratospheric ozone (NASA, 1979). In studying the history of model calculations of SST effects, the series of calculations made at Lawrence Livermore Laboratory is especially instructive (Luther, 1979; Weubbles _et al._, 1981). The Livermore group has considered one rate of NO_x injection (2000 molecules cm^{-3} s^{-1} spread out over a one kilometer band at either 17 or 20 km). This model injection is not intended to correspond to any particular SST fleet. They have calculated the change in ozone for these perturbations

for each of the many changes in photochemical constants and recognition of new important species over the period 1972-1981, Fig. 3. The primitive 1972 model gave a 33 percent ozone reduction. As stratospheric science was understood to be at the end of the Climatic Impact Assessment Program in 1975, this model gave a 10 percent ozone reduction. During the period 1976-1978, several rate coefficients were changed as improved experimental methods were used, and most of these changes reduced the calculated ozone reduction. During the period 1977 to mid-1980, the model calculated a new increase in the ozone column for NO_x injections at 17 and at 20 km.

It is well to pause and to check how well these models predict the natural stratosphere. Figure 4 shows the vertical column of nitric acid as a function of latitude for four seasons as calculated by a two-dimensional model (Widhopf and Glatt, 1979), and the Livermore calculated point at 30°N latitude is included. The figure also shows the observed vertical columns of nitric acid as obtained by several investigators and by several methods (reviewed by Johnston, 1981). The 1979 models greatly overpredict the amount of nitric acid in the stratosphere. Since most nitric acid occurs at altitudes below 30 km, this model failure applied primarily to the lower stratosphere. There are several other model failures in the range 15 to 30 km (NASA, 1979), and all of these failures seem to be in the direction of too much hydroxyl radical, HO, being calculated for the lower stratosphere.

During the summer and fall of 1980, new laboratory results were reported (Wine et al., 1980; Sridharan et al., 1980, Littlejohn and Johnston, 1980; Keyser, 1980) which show that HNO_3, H_2O_2, and $HOONO_2$

react with hydroxyl radicals much faster than previously indicated. The net effect of these new rate coefficients is that in 1981, the Livermore model again calculates a reduction of the ozone column by NO_x injections at 17 or 20 km, as is indicated by Fig. 3. In 1981 the predicted ozone decrease by the 20 km injection is about five percent (Wuebbles et al., 1981).

IV. Tests of Models Against Observations

It is desirable to check model predictions against known injections of NO_x in the real atmosphere and in each of the three regions of Fig. 2. It turns out that the historical records contribute partial tests of this kind.

(i) Ozone production in photochemical smog — Using simple, direct methods, Haagen-Smit and co-workers (1953) showed that ozone is produced by near ultraviolet radiation acting on almost any gas-phase organic molecule and nitrogen dioxide. Several examples showing ozone build-up and decay in both smog chambers and in the atmosphere were cited by Johnston and Quitevis (1975). The effect of NO_x on photochemical smog is complex, but it is abundantly illustrated that NO_x plus organic gases plus sunlight form ozone in the lower troposphere.

(ii) Ozone destruction by NO_x injection in the upper stratosphere by the solar proton event of August 1972 — The solar proton event of August 1972 injected a large amount of NO_x into the upper polar stratosphere over the period of a few days. One satellite measured the proton beam intensity above the atmosphere from which the injection of NO_x can be deduced, and another satellite measured the global ozone distribution of ozone in the upper stratosphere before and after the solar proton event (Crutzen *et al*, 1975; Heath *et al*., 1977). The Nimbus 4 satellite observed a large, conspicuous ozone reduction in the range of 35 to 50 km at 80°N, which persisted for many days. A recent comparison between calculated and observed ozone decreases is given by Fig. 5, using 1980 input parameters in a two-dimensional, time-dependent

stratospheric model (Solomon, 1980). It appears that current photochemical theory is fairly successful in predicting the effect of NO_x on ozone in the upper polar stratosphere.

(iii) Atmospheric nuclear bomb tests of 1961-62 — The nuclear bomb tests of 1961-62 injected a large, approximately known amount of NO_x into the lower stratosphere, and it has long been hoped that this injection could be used to calibrate the effect of NO_x in the lower stratosphere (Foley and Ruderman, 1973; Johnston *et al.*, 1973; Goldsmith *et al.*, 1973). For the NO_x injected by these nuclear-bomb tests, Chang and Duewer (1973) calculated the ozone reductions for the period 1957 to 1971. The maximum calculated effect was a four percent ozone reduction in 1963, which became two percent by 1966 and one percent by about 1968. When one considers the observed ozone columns at Arosa, Switzerland between 1926 and 1970, for example, the noise in these records is so large that an effect the size and shape of Chang and Duewer's function is lost (Birrer, 1974). The monthly deviations of the Arosa ozone record from the 40 year monthly means are compared with the theoretical ozone-decrease function in Fig. 6. The natural variation of ozone is so great that one can neither prove nor disprove the presence of an ozone perturbation, plus or minus, like the one calculated by Chang and Duewer (Johnston, 1981).

V. Conclusions

The relation of supersonic transports to stratospheric ozone has a political history as well as a scientific history, but I am not especially going into that area. In this case history, I think a distinction should be made between using scientific considerations to call for an environmental impact assessment and in contending there is scientific proof for certain effects or lack of effects. In 1970 with respect to water and in 1971 with respect to nitrogen oxides, there were ample scientific grounds to call for an environmental impact study concerning the effect of large SST fleets on stratospheric ozone. When public policy decisions on a problem involving science must be made at a particular time, the decision has to be made on the basis of the scientific knowledge available at that time. For example, the U.S. Congress in 1971 mandated that the Climatic Impact Assessment Program submit its final report by the end of 1974; and thus the report reflected the status of the subject in 1974, not necessarily what the community of scientists would regard as a proven case.

If this topic is examined as a field of science, one sees a history of many dedicated workers in the laboratory, in the atmosphere, and at the computer. One sees the evolution of this field from its primitive state in 1970 to that of an active, developing science in 1981. Even now, I think, the field is not mature. We can identify features that are unknown or are poorly characterized, especially in the 15 to 30 km altitude range. Although much progress has been made in selecting and studying photochemical reactions in the laboratory, more effort is needed toward obtaining a complete list of the important atmospheric

species and accurately measuring all appropriate rate coefficients. One looks forward to satellite data for a global inventory of some important trace species. One anticipates continued improvement of two and three dimensional models of atmospheric motions.

With respect to stratospheric ozone, one could not in 1970 and cannot at this time prove that it is safe for large fleets of supersonic aircraft to operate in the stratosphere, and on the other hand one could not then and cannot now prove that it is unsafe. However, the problem appears to be a finite one, and I expect that within another 10 years scientists of the stratosphere will be able to provide a clear-cut answer to this question.

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Figure Captions

Figure 1. History of the perceived value of the rate coefficient for reaction (5):

$$HO + O_3 \rightarrow HOO + O_2$$

Hunt (1966); Langley and McGrath (1971)

1973-1979: Δ, critical reviews; O, measurements.

Figure 2. Comparison between the calculated local rate of ozone destruction by the NO_x catalytic cycle and ozone formation rate from the methane-NO_x-smog reactions (Johnston and Quitevis, 1974, 1975).

Figure 3. History of the calculated change in the ozone vertical column for standard nitric oxide injections at 17 and 20 km as calculated by the Lawrence Livermore Laboratory one-dimensional model (Luther, 1979; private communication, 1981). These calculations were made with the same model for atmospheric motions, but they vary with changed perceptions in how to treat solar radiation, in identity of important atmospheric species, and in values of photochemical rate coefficients.

Figure 4. Observed and calculated vertical columns of nitric acid in the stratosphere as a function of latitude and season. The curves were calculated by Widhoff and Glatt's (1979) two-dimensional model. The cross was calculated by the Livermore 1-D model. Aircraft observations: O, January 1974; Δ, April 1974. Balloon observations: □, for different authors and seasons as described by Johnston (1981).

Figure 5. Calculated and observed decrease in ozone, eight days after the solar proton event of August 1972. The calculation was done by Solomon (1980) using Crutzen's two-dimensional model and photochemical coefficients as of late fall 1980.

Figure 6. Monthly deviations of observed ozone from the 40 year mean of each month at Arosa, Switzerland as reported by Goldsmith et al. (1973) in the upper panel. The calculated ozone reduction from the nuclear bomb tests by Chang and Duewer (1973) is given to the same scale in the small figure between 1957 and 1970 between the two panels. The lower panel is the same as the upper panel with the points displaced downward according to Chang and Duewer's function. The calculated ozone reduction is submerged by the large natural variation so that no conclusion, one way or another, can be drawn from this comparison.

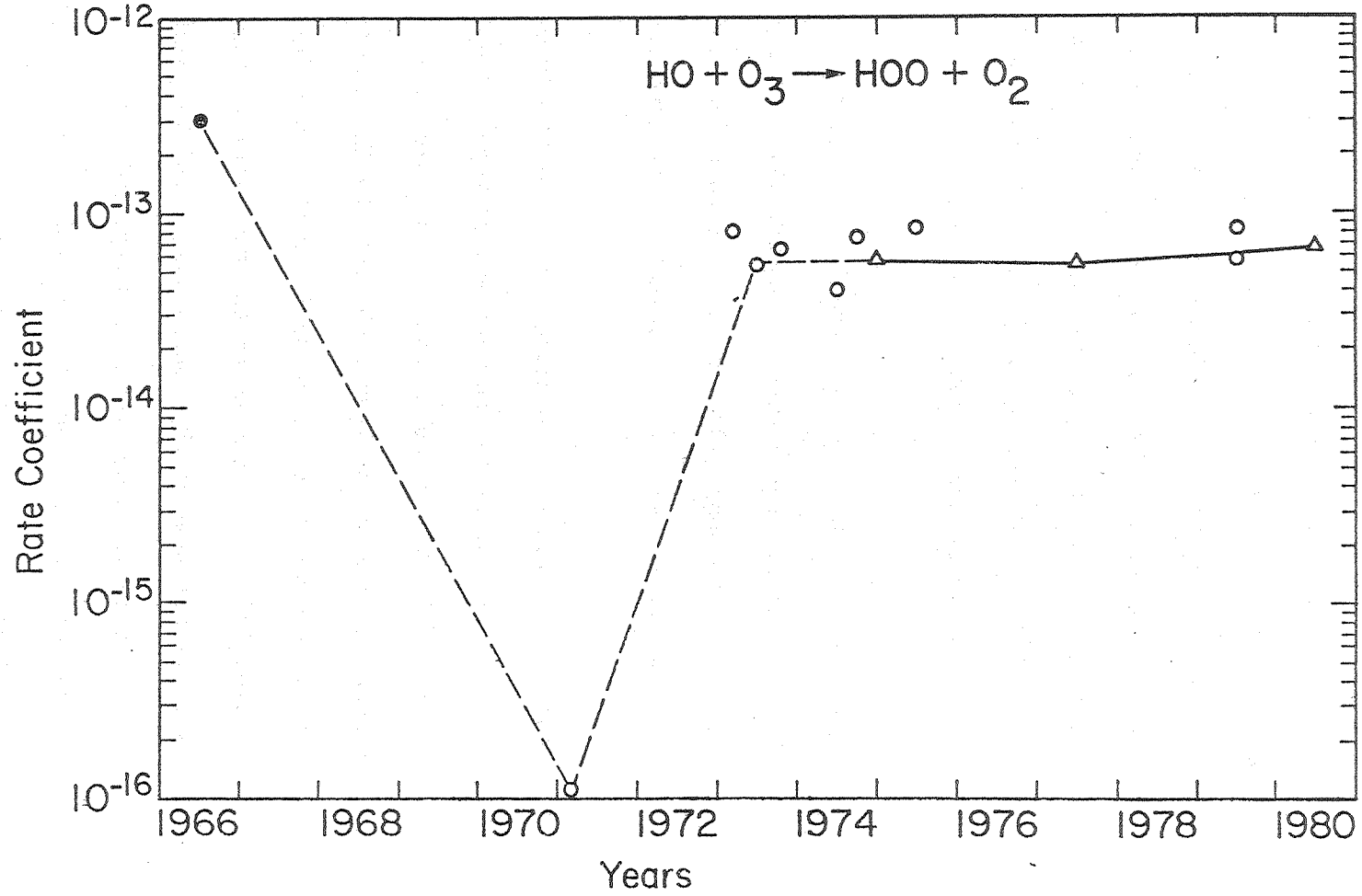
$HO + O_3 \rightarrow HOO + O_2$
Rate Coefficient
10^{-12}
10^{-13}
10^{-14}
10^{-15}
10^{-16}
1966
1968
1970
1972
1974
1976
1978
1980
Years

Fig. 1

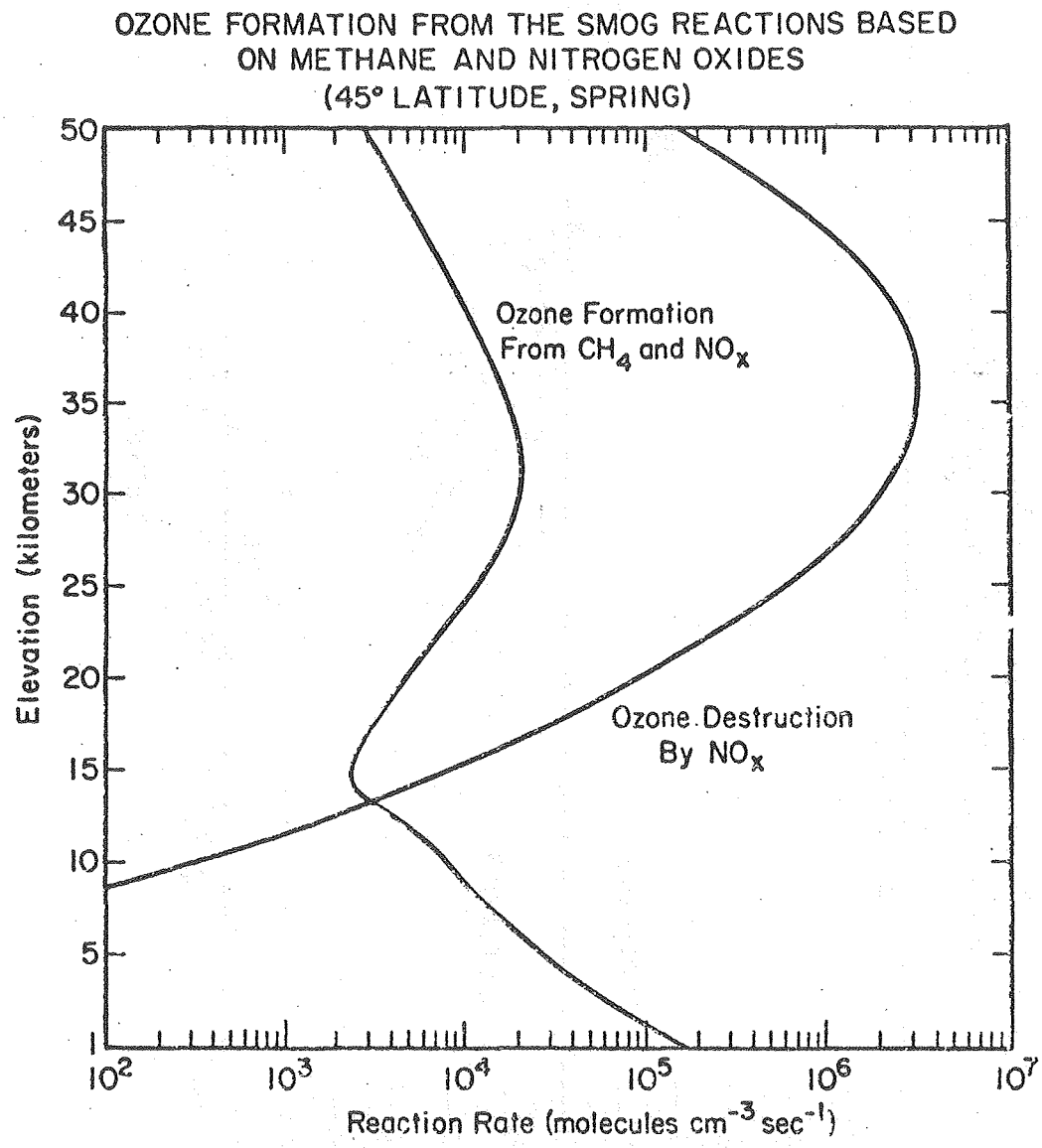
OZONE FORMATION FROM THE SMOG REACTIONS BASED
ON METHANE AND NITROGEN OXIDES
(45° LATITUDE, SPRING)
Ozone Formation
From CH_4 and NO_x
Ozone Destruction
By NO_x
Elevation (kilometers)
50
45
40
35
30
25
20
15
10
5
1
10^2
10^3
10^4
10^5
10^6
10^7
Reaction Rate (molecules cm^{-3} sec^{-1})

Fig. 2

CALCULATED OZONE-COLUMN REDUCTION FOR STANDARD NO_x INPUT BY LIVERMORE ONE-DIMENSIONAL MODEL

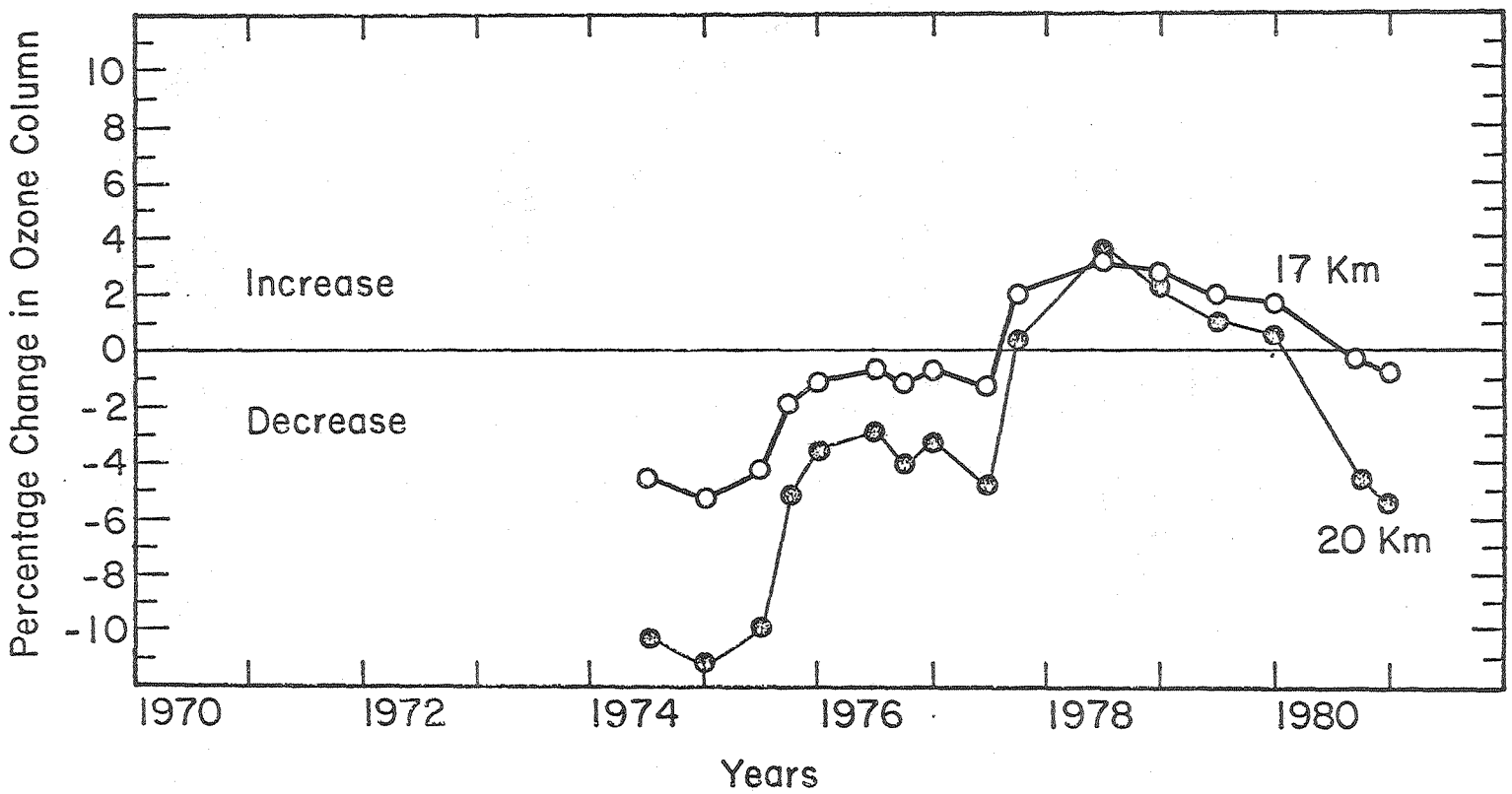

Fig. 3

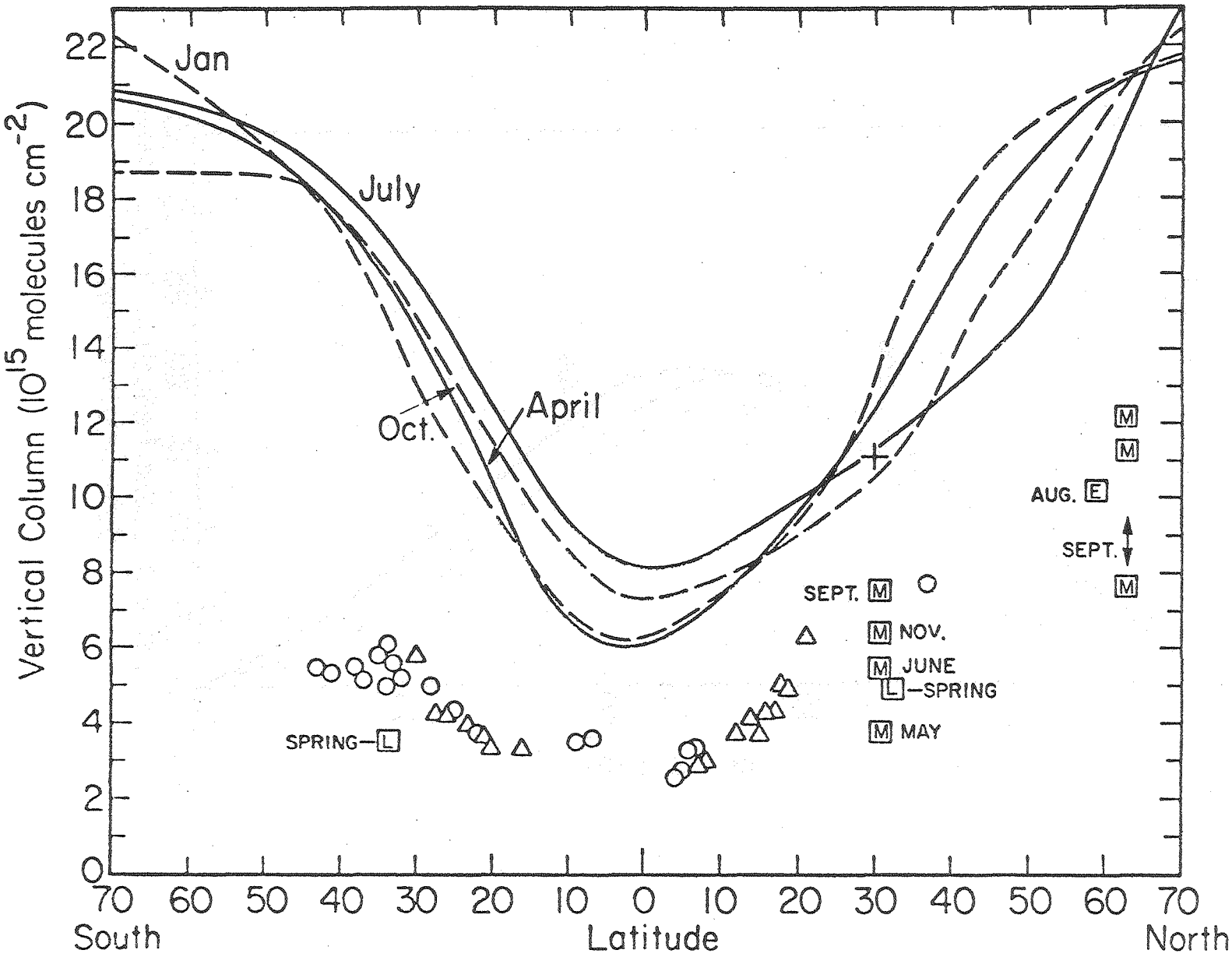
Vertical Column (10^{15} molecules cm^{-2})
22
20
18
16
14
12
10
8
6
4
2
0
Jan
July
April
Oct.
SPRING—L
SEPT. M
NOV.
M JUNE
L—SPRING
M MAY
M
M
AUG. E
SEPT.
M
70 60 50 40 30 20 10 0 10 20 30 40 50 60 70
South
Latitude
North

Fig. 4

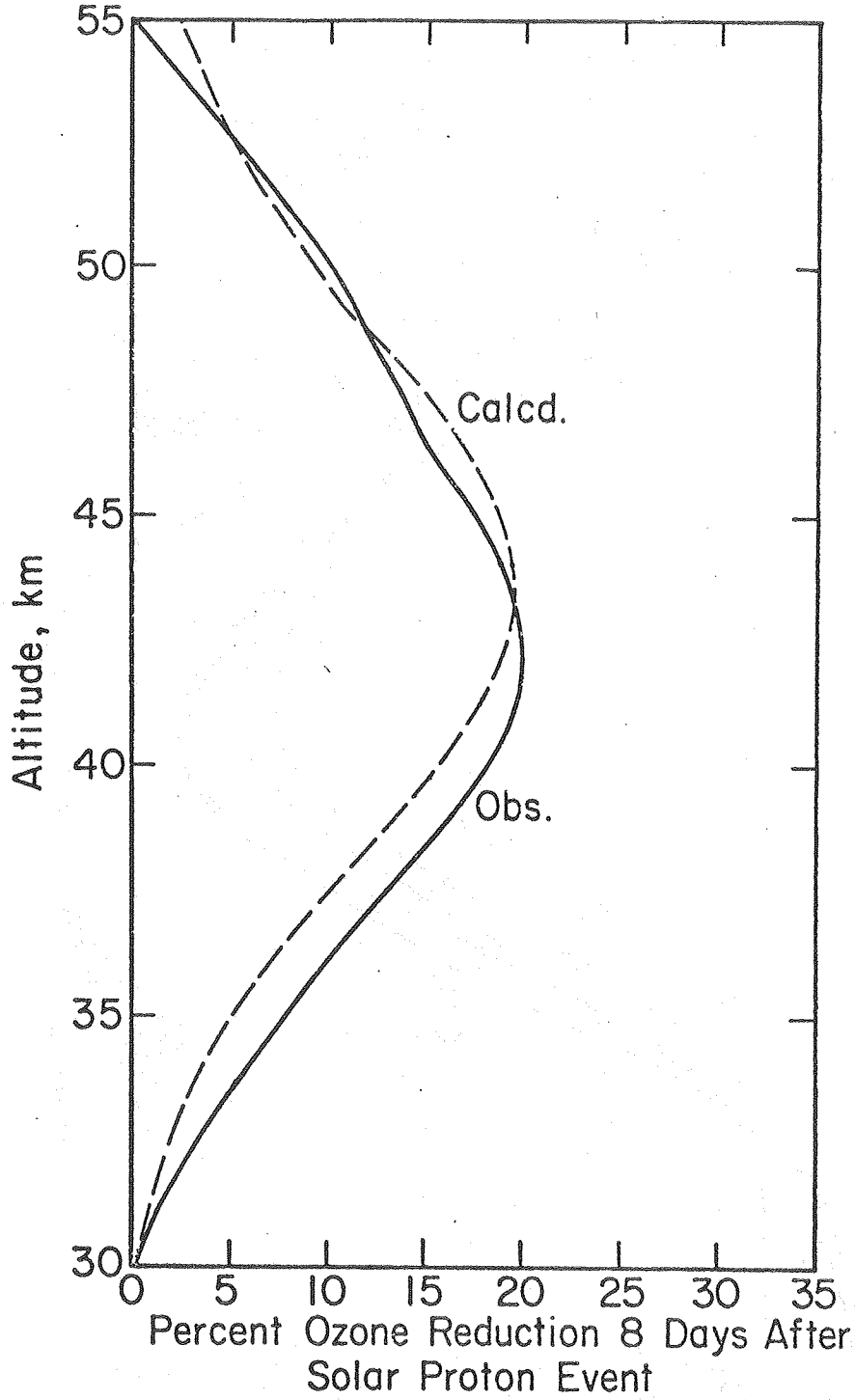
55
50
45
40
35
30
Altitude, km
Calcd.
Obs.
0
5
10
15
20
25
30
35
Percent Ozone Reduction 8 Days After
Solar Proton Event

Fig. 5

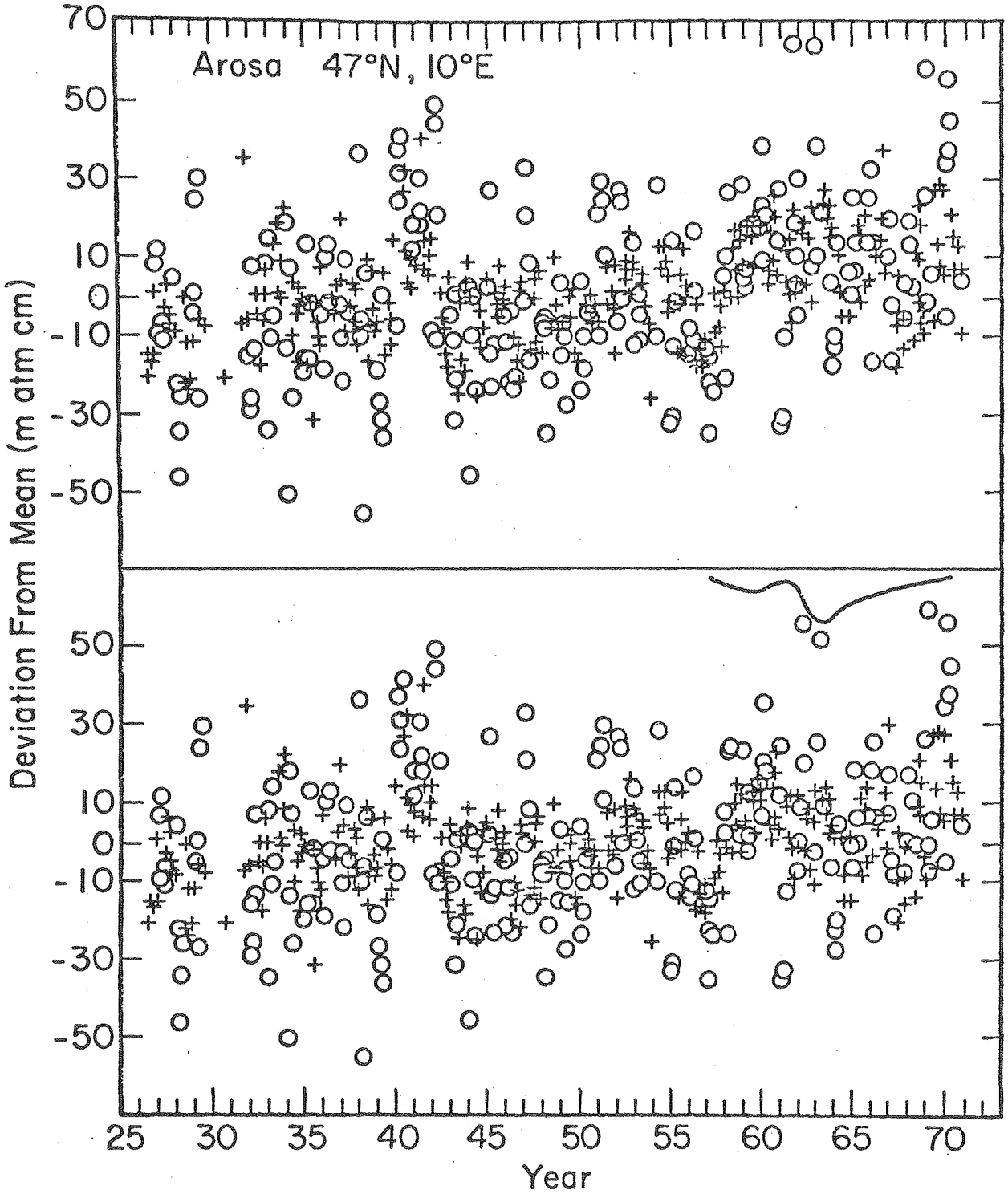

Fig. 6

XBL 7311-6739