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**Author**
Johnston, Harold S.

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Presented at the Conference on the
Climatic Impact Assessment Program,
Cambridge, MA, February 26 - March 1, 1974

LBL-2753

# ALTERNATIVE INTERPRETATION OF UMKEHR DATA FOR NITROGEN DIOXIDE

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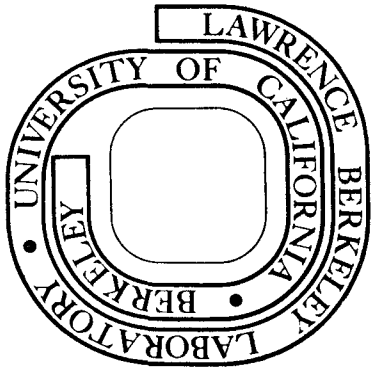


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# Alternative Interpretation of Umkehr Data for Nitrogen Dioxide

by

Harold S. Johnston

Department of Chemistry and
Inorganic Materials Research Division,
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

## Abstract

Brewer and coworkers (1973) have successfully overcome the difficulties of observing atmospheric nitrogen dioxide from its visible absorption spectrum. They have developed a method (related to the ozone umkehr method), which should be very valuable in monitoring both tropospheric and stratospheric $NO_2$. The first set of data that they have published (Nature, 1973) is capable of alternative interpretations: (1) Brewer et al assumed that $NO_2$ was constant during and shortly after sunrise and sunset, from which they deduced the vertical distribution of $NO_2$, and they deduced a very high maximum value of $NO_2$ at midday; (2) alternatively, the data may be interpreted in terms of rapidly changing $NO_2$ at sunrise and sunset, a slow smooth increase during the day, and no midday maximum. The second interpretation is consistent with current chemical models of the stratosphere.

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## Introduction

Nitrogen dioxide ($NO_2$) has a strong, highly structured absorption spectrum in the visible and near ultraviolet spectral region; a portion of this spectrum is shown in Figure 1. It would appear that this detailed spectrum could be used to observe nitrogen dioxide in the atmosphere, but several workers have reported failure to do so (Informal reports and verbal communications). Difficulties include Rayleigh scattering, particulate scattering, atmospheric inhomogenieties, and the highly structured solar spectrum in the same wavelength region, Figure 2. Brewer, Kerr, and McElroy (BKM, 1973; BMK, 1974) have surmounted these difficulties by an ingenious differential method including a sensitive photon-counting technique. BKM used three wavelengths at a peak and two valleys of the $NO_2$ absorption, Figure 1, where $\lambda_1$ = 0.4377 μm, $\lambda_2$ = 0.4448 μm, and $\lambda_3$ = 0.4500 μm. They looked directly at the sun for one series, and they looked at scattered light from the zenith sky for another group of measurements. Their spectral resolution was about 0.0030 m. They defined the function F

$$F = \log \frac{I_1}{I_2} + 1.46 \log \frac{I_3}{I_2} \qquad (1)$$

The constant 1.46 was selected to eliminate (to a high degree of approximation) the effect of Rayleigh scattering. Particulate scattering changes smoothly in this wavelength region (in some cases as $\lambda^{-1.8}$, Charlson and Ahlquist, 1969), and the effect on $\log I_1/I_2$ is very nearly cancelled by the opposite effect on $\log I_3/I_2$.

Ozone also has a structured spectrum in this wavelength region, but its effect is readily calculated and is small. One assumes that $NO_2$ and $O_3$ obey the relation $\ln I_o/I = \sigma C$, where $\sigma(cm^2)$ is the observed

wave-length-dependent light-absorption cross section and C is the column of $NO_2$ or $O_3$ in units of molecules $cm^{-2}$. The function F then is

$$F = F_o + 2.78\times10^{-23}\, C^\circ_{O_3} \sec x + 3.04\times10^{-19}\, C^\circ_{NO_2} \sec x \quad (2)$$

$$F_o = \log \frac{I_{01}}{I_{02}} + 1.46 \log \frac{I_{03}}{I_{02}} \quad (3)$$

where $C^\circ$ is the vertical column, x is the solar zenith angle, and $I_{01}$, $I_{02}$, $I_{03}$ are the solar intensities above the atmosphere. (Strictly speaking, sec x should be replaced by a more complex term acknowledging curvature of the earth for values of sec x in excess 8). A vertical column of 0.33 cm(STP) of ozone gives the same value of F as a vertical column of $NO_2$ of $0.8\times10^{15}$ molecules $cm^{-2}$, a small correction easily applied to the observed data. After this correction is applied, one has two ways to evaluate the $NO_2$ vertical column from ground-based (or aircraft based) observations. The slope of F with sec x gives a direct, self-calibrating measure of the vertical column of nitrogen dioxide

$$C^\circ_{NO_2} = (dF/d \sec x)/3.04\times10^{-19} \quad (4)$$

provided that the vertical column itself does not change very much during the time of change of the solar angle to give d sec x. In an alternate method the value of F is observed over a wide range of values of sec x for one day, extrapolated to zero sec x, and the value of $F_o$ inferred for use on that and other days. In this case every measurement of F is a direct measurement of the vertical column of $NO_2$

$$C^\circ_{NO_2} = \frac{F-F_o}{3.04\times10^{-19} \sec x} \quad (5)$$

provided that $F_o$ is constant. The highly structured solar spectrum, Figure 2, puts very great demands on the rigidity and constancy of the wavelengths settings of the spectrograph; a very slight change of wavelength settings, especially for $\lambda_2$, can cause a large change in $F_o$.

BKM came to four conclusions: (1) The method can overcome the difficulties of light scattering and ozone absorption to give a measure of the $NO_2$ column; (2) the nitrogen dioxide column increased by about factor of 1.5 between early morning and late afternoon; (3) the nitrogen dioxide column showed a midday maximum about a factor of 3 greater than the morning value; and (4) observations of the vertically scattered zenith radiation through sunrise or sunset give information about the vertical distribution of $NO_2$ in the atmosphere. In this article evidence is presented in support of BKM's conclusions (1) and (2), and it is argued that alternative interpretations can be given to their conclusions (3) and (4).

## Evaluation of $F_o$

BKM measured the value of F by focussing on the sun from sunrise through noon to sunset on August 3, 1973 at Toronto, Ontario, Canada. Their results are replotted and presented in Figure 3. The early morning points do not coincide with the late afternoon points, and thus the overhead column of $NO_2$ changed during the day. This change of the column of $NO_2$ during the day makes difficult and uncertain the extrapolation to zero sec x in order to evaluate $F_o$, Equation 2. The function, sec x, changes rapidly near sunrise and near sunset but only very slowly during the middle of the day; for example, 3 units of sec x from 7.9 to 4.9 requires 27 minutes, 3 units from 4.9 to 1.9 requires 123 minutes, and 0.7 units from 1.85 to 1.15 requires 184 minutes. BKM

reasoned that less change of $NO_2$ would be expected during the 45 minute interval shown in Figure 3 of early morning or late afternoon, as opposed to the long period to obtain a comparable change of sec x during the middle of the day. Thus they graphically extrapolated the points from sec x = 11.5 to sec x = 5.5 to zero, Figure 3. This value of $F_o$ was used in all cases in the 1973 article by BKM. Their conclusions depend critically on the value of $F_o$ so obtained.

One contention of this article is that the extrapolation to obtain $F_o$ is not precise; it is subject to considerable error and uncertainty. BKM gave several other sets of data which can be extrapolated to give $F_o$; two examples are given in Figures 4 and 5. Figure 4 gives ground-based values of F for early morning of July 23, 1973; and Figure 5 gives late afternoon data obtained from an airplane at 12 km elevation on June 13, 1973. These data cover the same range of sec x as that used by BKM to obtain $F_o$ from the data of August 3. The value of $F_o$ can be obtained from the observed data on June 13 (PM), July 23 (AM and PM), and August 3 (AM and PM).

These 5 sets of data were fit to the equation

$$F = F_o + K \sec x$$

by the method of least squares for sec x between 5.5 and 12. The results are shown in Figure 6 and the intercepts $F_o$ are given in Table 1. The intercepts $F_o$ vary as -0.003, 0.009, 0.010, 0.013, 0.019. The spread from -0.003 to +0.019 is 0.022 units of F, and this corresponds to a vertical column of $72 \times 10^{15}$ molecules of $NO_2$ per square cm, which corresponds to 18 parts per billion above 12 km. Thus the uncertainty in $F_o$ as measured by these 5 cases from BKM (1973) is very large.

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The effect of this uncertainty is especially great with respect to interpretation of the midday data.

The data of Figure 3 for August 3 can be extrapolated to zero in at least two different ways, each of which is plausible. One method is that used by BKM, as discussed above, and another method is proposed here. Although the afternoon data in Figure 3 all lie above the morning data, the difference is attenuated by the large values of sec x, and the absolute value of the difference is not great. The extrapolation to zero sec x could quite reasonably use all of the data of Figure 3. The least squares straight line through all the data are given as curve A in Figure 7. In units of the previous figures, the value of $F_o$ is 0.0186. The extrapolation used by BKM is given as lines B and C in Figure 7. The two lines D are derived from Figure 8.

The column of $NO_2$ calculated from Equation 5 for a given value of F depends strongly on the value of $F_o$ used. All of the experimental data are plotted twice in Figure 8. In one case (points represented by crosses) the value of $F_o$ is 0.0186 as found from extrapolation A in Figure 7. The points give a vertical column of $NO_2$ of about $22 \times 10^{15}$ molecules $cm^{-2}$ in the early morning, about $26 \times 10^{15}$ at noon, and about $30 \times 10^{15}$ in the late afternoon. The least squares line A in Figure 7 is the flat line A in Figure 8. The morning points systematically lie below the line and the afternoon points systematically lie above the line. A better description of the crosses in Figure 8 is the straight line D, which slowly and linearly increases from morning to sunset. This line is used to calculate the function F from $F_o$ as found by curve A; the calculated F curve is replotted as the third case, D, in Figure 7. In both Figures 7 and 8, the lines D give an excellent representation of the data.

The column of $NO_2$ was also calculated from each data point using the value of $F_o$ as obtained by BKM, and these values are the circles in Figure 8. The extrapolated lines B and C from Figure 7 are seen between 5 and 6 AM and between 6 and 7 PM. With this value of $F_o$, the calculated midday $NO_2$ increases to a high broad maximum, Figure 8, which is about three times greater than the early morning value. It is to be emphasized that the circles and crosses of Figure 8 are based on the same experimental data, Figure 3. The difference between the two sets of points is the value of $F_o$ used in Equation 5 to go from observed F to calculated $NO_2$ column. The evaluation of $F_o$ as given by line A of Figure 7 gives the crosses in Figure 8, and the evaluation of $F_o$ as given by B and C of Figure 7 gives the circles in Figure 8. Whether $NO_2$ goes through a midday maximum or shows a simple monotonic increase from morning to sunset depends critically on how F is extrapolated to zero sec x, and this extrapolation shows poor precision from one case to another, Figure 6.

## Evaluation of $NO_2$ from Slopes

The value of the column of nitrogen dioxide can be calculated from the slope of the value of F as a function of sec x, Equation 4. To evaluate $C^{\circ}_{NO_2}$ from Equation 4, it is only necessary for the instrument to be stable for an hour or so, whereas to evaluate $C^{\circ}_{NO_2}$ from Equation 5, one must have atmospheric and instrumental stability to give a reproducible $F_o$ day after day. The values of the $NO_2$ column inferred from the slopes of Figure 6 and Equation 4 are given in Table 1. The slopes are corrected for 0.33 cm of ozone. The values on June 13 were directly observed at 12 km. On August 3, a second instrument was put on board an airplane and F was observed up to and back down from 12 km

at midday. The difference in F between 12 km and ground was about 0.008 units (BKM's Figure 7), which corresponds to $26.3 \times 10^{15}$ molecules $NO_2$ $cm^{-2}$. This value was subtracted from the ground based values found in the morning and late afternoon, and the results are entered in Table 1. These values consistently indicate stratospheric columns of $NO_2$ of about $(4\pm2) \times 10^{15}$ molecules $cm^{-2}$, with larger values in the afternoon than in the early morning. This value can be compared with the global average nitric acid column of $4 \times 10^{15}$ molecules $cm^{-2}$ as reported by Lazrus and Gandrud (1974). Model calculations, for example Isaksen (1973), show that columns of species $HNO_3/NO_2/NO$ occur at 45°N in the summer in the ratio 4/3/3. Thus the values of stratospheric $NO_2$ as inferred by slopes of Brewers F function are in good agreement with models and with observations of stratospheric nitric acid.

## The Diurnal Trend of Nitrogen Dioxide

During the day there is a dynamic balance between NO, $NO_2$, $NO_3$, $N_2O_5$, and $HNO_3$, which is brought about by photolysis and by reactions of these species with O, $O_3$, HO, HOO. At sunset, the photolyses cease, and the species O, HO, and HOO decrease to very small values. Nitric oxide rapidly reacts with ozone and with $NO_3$

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$NO + NO_3 \rightarrow 2\ NO_2$$

This conversion is virtually complete within a few minutes in the stratosphere. Nitrogen dioxide slowly reacts with ozone

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

$$NO_3 + NO_2 \xrightarrow{M} N_2O_5$$

and depending on the temperature and concentration of ozone, more or less half of the $NO_x$ is converted to $N_2O_5$ during the night (Johnston, 1971).

Dr. Gary Whitten carried out a model calculation of the diurnal variation of 12 species involving odd oxygen, the oxides and oxyacids of nitrogen, and free radicals based on water oxygen, and including 45 elementary chemical reactions. A standard distribution (45°N, spring equinox) of ozone, water, and temperature (Johnston and Whitten, 1973) was taken. The total $NO_x$ column (NO, $NO_2$, $NO_3$, $N_3O_5$, $HNO_3$) was $14 \times 10^{15}$ molecules $cm^{-2}$, and the vertical distribution of each species was derived. The distribution of sunlight was recomputed each hour of the day. The diurnal variation of these $O_x$, $NO_x$, and $HO_x$ species was obtained at any time t and t + 24 hours. The results of the integrated vertical column of $NO_2$ from 15 to 50 km is given by Figure 9 for a period of 26 hours. During the night $NO_2$ is slowly converted to $N_2O_5$. At sunrise about half of the $NO_2$ is quickly converted to nitric oxide

$$NO_2 + h\nu \rightarrow NO + O \xrightarrow{O_2} NO + O_3$$

$$NO + O_3 \rightarrow NO_2 + O_2$$

The relaxation times for this process varies between 30 to 90 seconds depending on elevation. During the day $NO_2$ is slowly formed from the photolysis of $N_2O_5$

$$N_2O_5 + h\nu \rightarrow 2\ NO_2 + \tfrac{1}{2}\ O_2 \text{ (mechanism uncertain)}$$

with a relaxation time of about 1 hour at 40 km to about 8 hours at 15 km. For this model calculation, the vertical column of $NO_2$ increased from $3.5 \times 10^{15}$ an hour after sunrise to $5.9 \times 10^{15}$ at sunset. This calculated change is in good agreement with Brewer's observations, if

one uses the value of $F_o$ as derived from line A in Figure 7.

There is a rapid change of $NO_2$ and NO immediately after sunrise or sunset. An example of the changes of NO, $NO_2$, and $N_2O_3$ for 3 minutes after sunrise is given by Figure 10 for an elevation of 33 km. BKM (1973) observed the scattered light from the zenith sky through sunrise and sunset (BKM's figures 2A and 2B, for example). These observations were used to infer the vertical distribution of $NO_2$. However, as can be seen from Figures 9 and 10, it is at sunrise and sunset that $NO_2$ changes most rapidly of any time of day. The rapid decrease of $NO_2$ after sunrise ($NO_2 + h\nu \rightarrow NO + O$) and the rapid increase of $NO_2$ after sunset ($NO + O_3 \quad NO_2 + O_2$) invalidate the use of scattered zenith radiation at these times as a measure of the vertical distribution of $NO_2$.

## Acknowledgement

This work was supported by the Climatic Impact Assessment Program by means of an interagency agreement between the Department of Transportation and the U.S. Atomic Energy Commission through the Inorganic Materials Research Division, Lawrence Berkeley Laboratory.

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## Titles to Figures

Figure 1 - Portion of visible absorption spectrum of nitrogen dioxide as observed in this laboratory showing the three wavelengths used by BKM to define the function F.

Figure 2 - High resolution display of solar spectrum as measured at the Earth's surface in the wavelength vicinity of BKM's three points.

Figure 3 - A replotting of data from Figure 6 of BMK (1974). The value of $F_o$ is obtained by extrapolation of the data in the 45 minute range identified by the arrows. August 3, 1973.

Figure 4 - Data replotted from Figure 3a of BMK (1974). July 23, 1973.

Figure 5 - Data replotted from Figure 3 of BKM (1973). June 13, 1973.

Figure 6 - Evaluation of $F_o$ from 5 sets of data from BKM (1973) over the same range of sec x as used by BKM in their extrapolation to obtain F.

Figure 7 - Three replottings of the data from Figure 6 of BMK (1974). A, extrapolation to zero sec x using all of the data. B, C extrapolation to zero sec x as done by BMK. D. Curves deduced from line D in Figure 8, based on intercept from line A above.

Figure 8 - Computed variation of vertical column of $NO_2$ (August 3, 1973) during the day on the basis of two different values of $F_o$ (A and BC of Figure 7). These computed points are derived from the same observed values of F; they differ only as to value of $F_o$ used. The line D represents a linear increase of $NO_2$ from 30 minutes after sunrise to sunset; it gives the values of F in curves D of Figure 7 if one uses to $F_o$ from curve A of Figure 7.

Figure 9 - Diurnal variation of the $NO_2$ vertical column as calculated from a chemical model of 12 species ($O_x$, $HO_x$, $NO_x$) and 55 elementary reactions. The calculations were carried out by Dr. G. Whitten.

Figure 10 - The calculated changes of NO, $NO_2$, and $N_2O_5$ at 33 km. during three minutes after sunrise (These fast changes after sunset and sunrise are not shown in detail in Figure 9).

Table 1. - The Intercept $F_o$ and the Vertical Column of $NO_2$ Inferred from the Slope, dF/d sec x.

| Observation | $F_o$ | Vertical column of $NO_2$, $10^{15}$ molecules $cm^{-3}$ | | |
|---|---|---|---|---|
| | | From slope | Corrected for $O_3$ | Above 12 km |
| June 13, PM | +0.013 | 4.6 | 3.8 | 3.8 |
| July 23, AM | +0.010 | 7.4 | 6.6 | |
| July 23, PM | +0.019 | 10.2 | 9.4 | |
| August 3, AM | -0.003 | 30.1 | 29.2 | 2.9* |
| August 3, PM | +0.009 | 33.7 | 32.9 | 6.6* |

*Corrected for 0.008 F units between 0 and 12 km on basis of BKM's Figure 7.

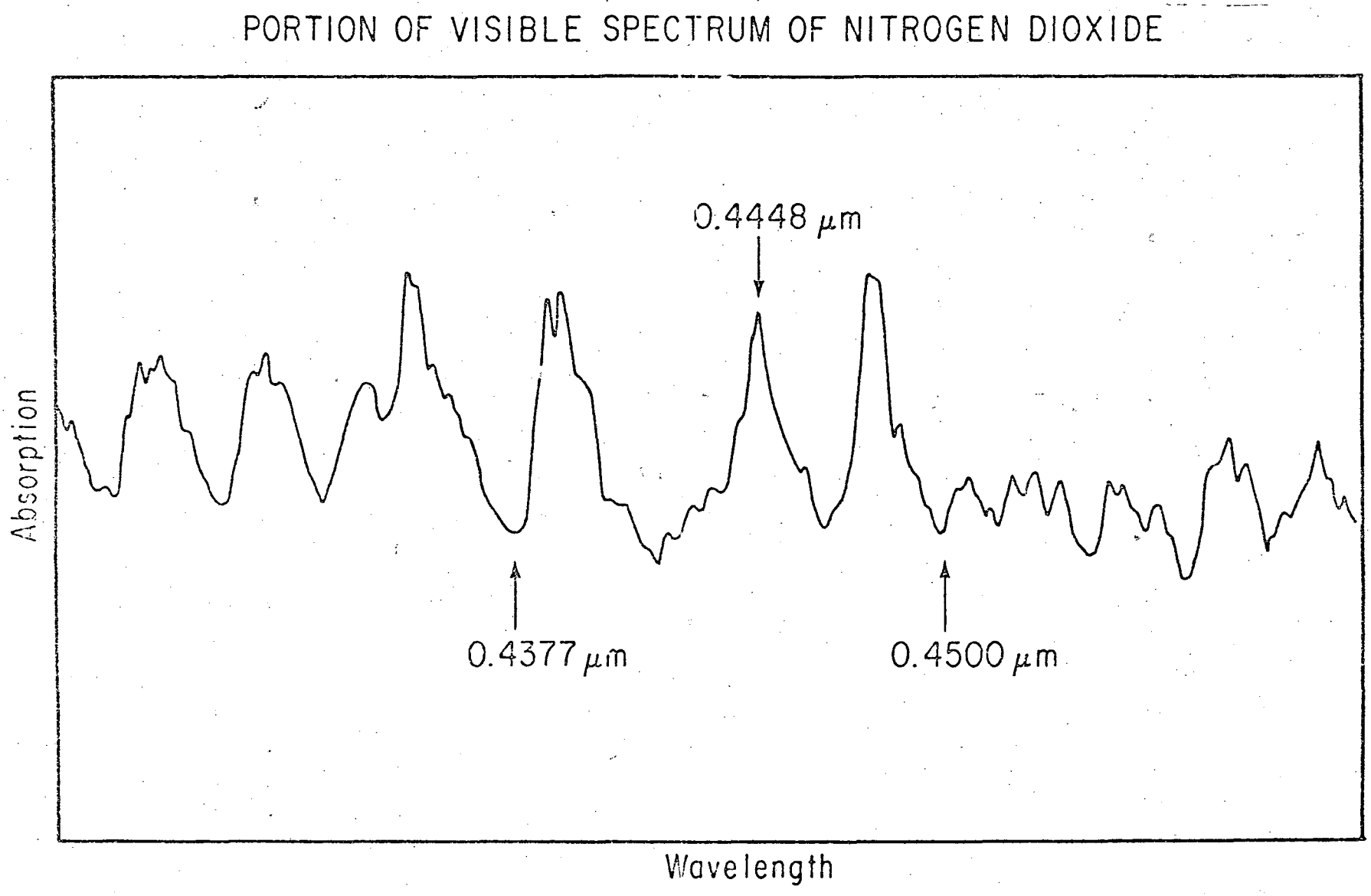


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Fig. 1

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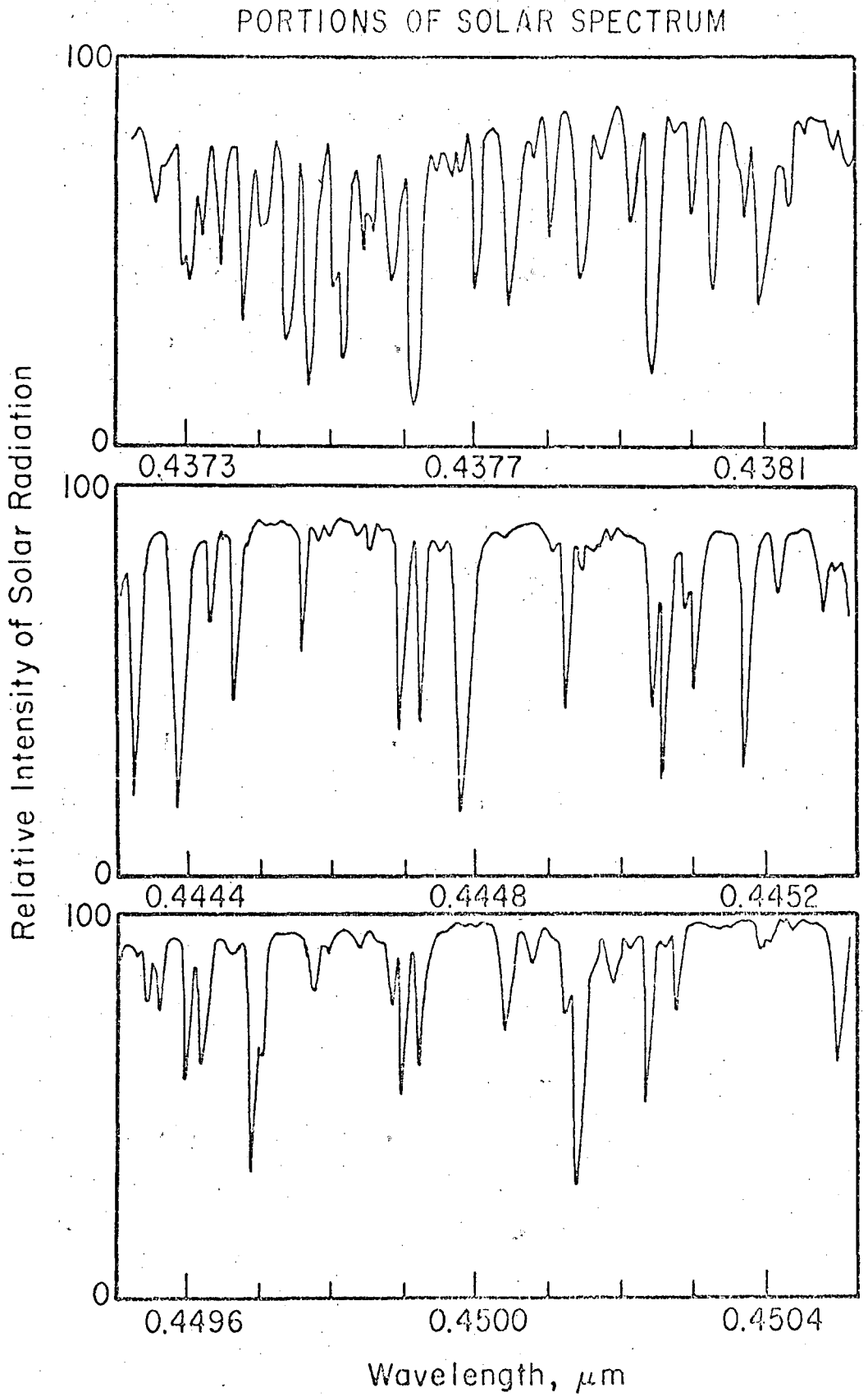


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Fig. 2

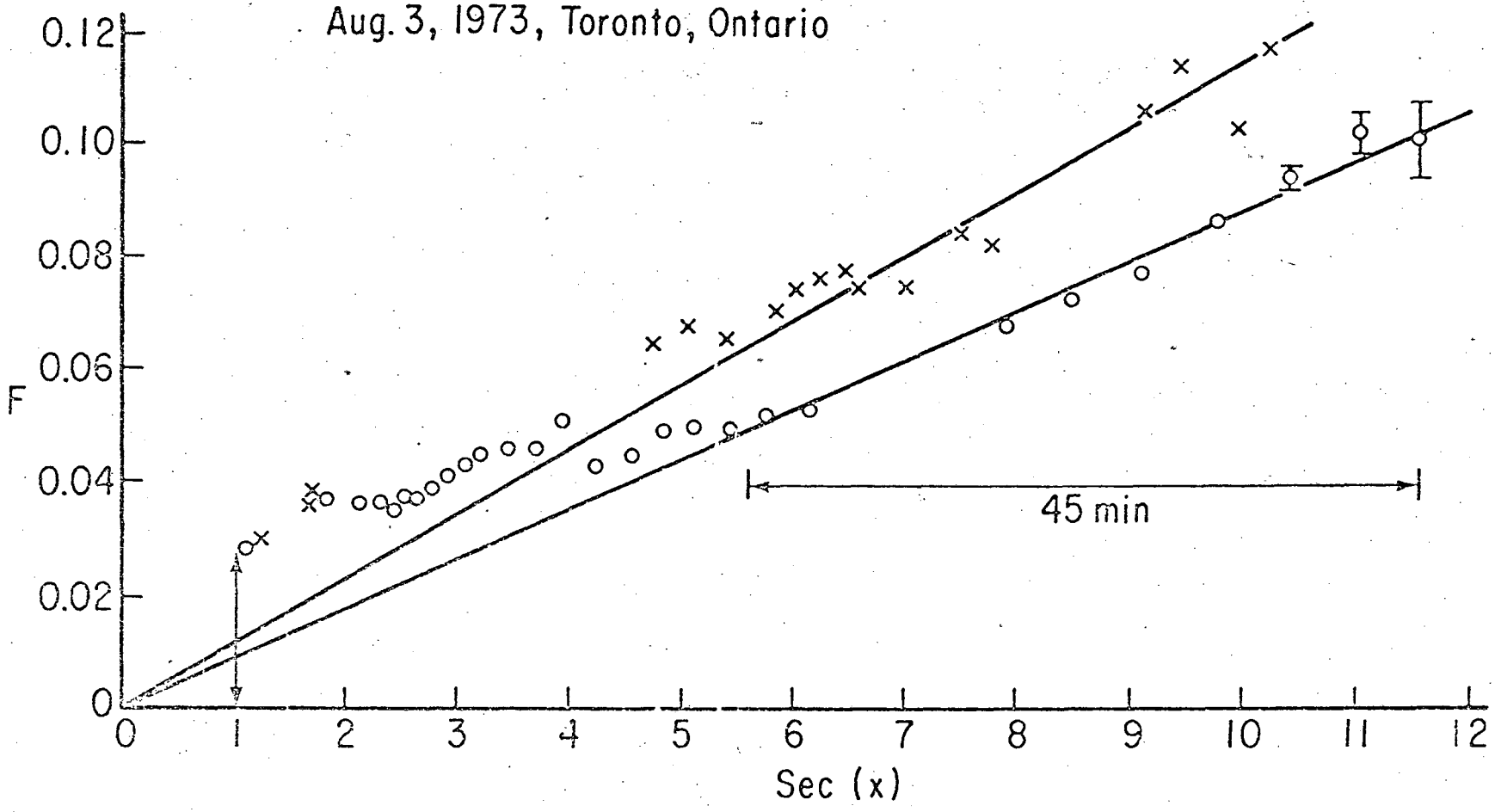


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Fig. 3

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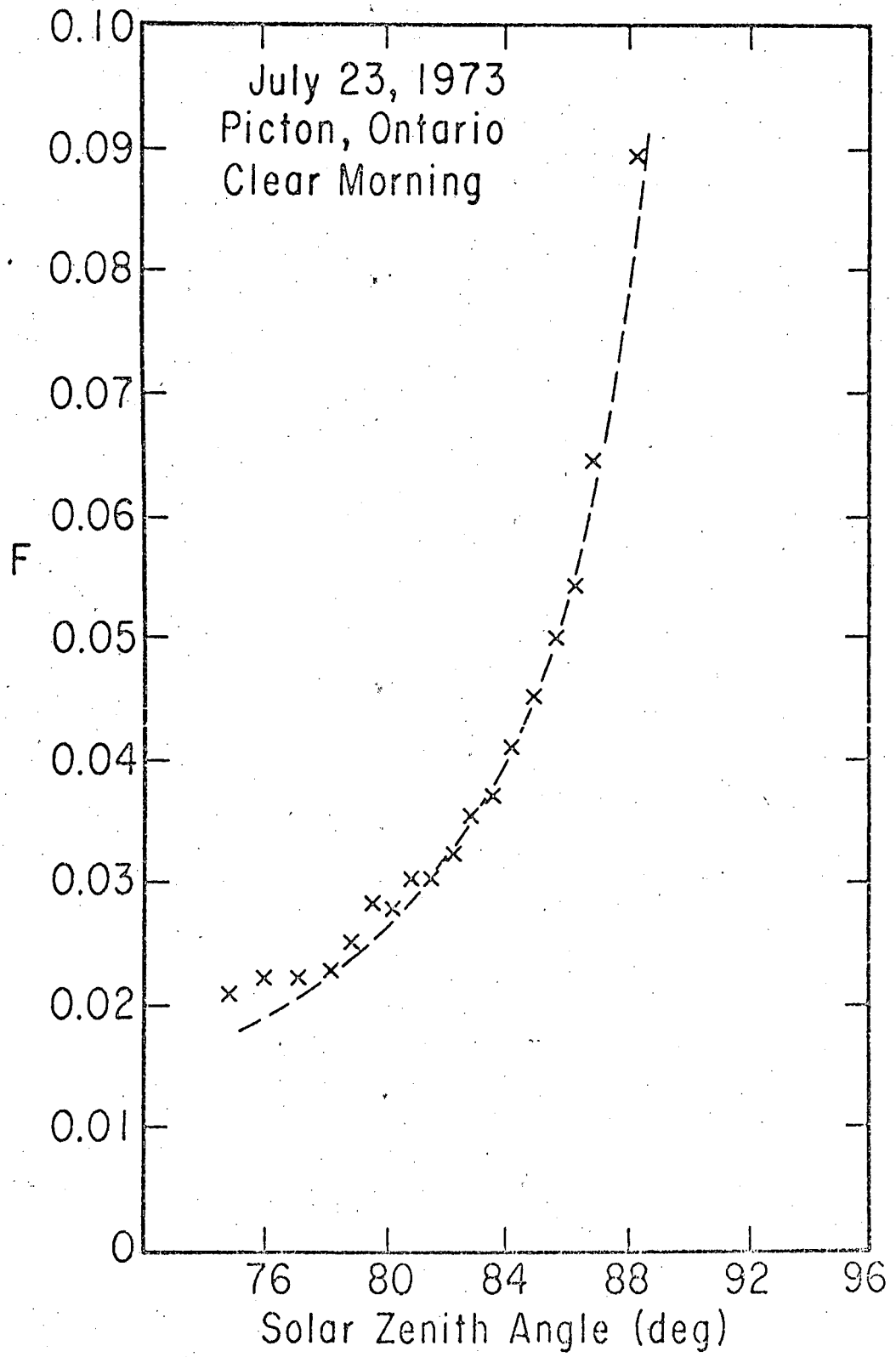


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Fig. 4

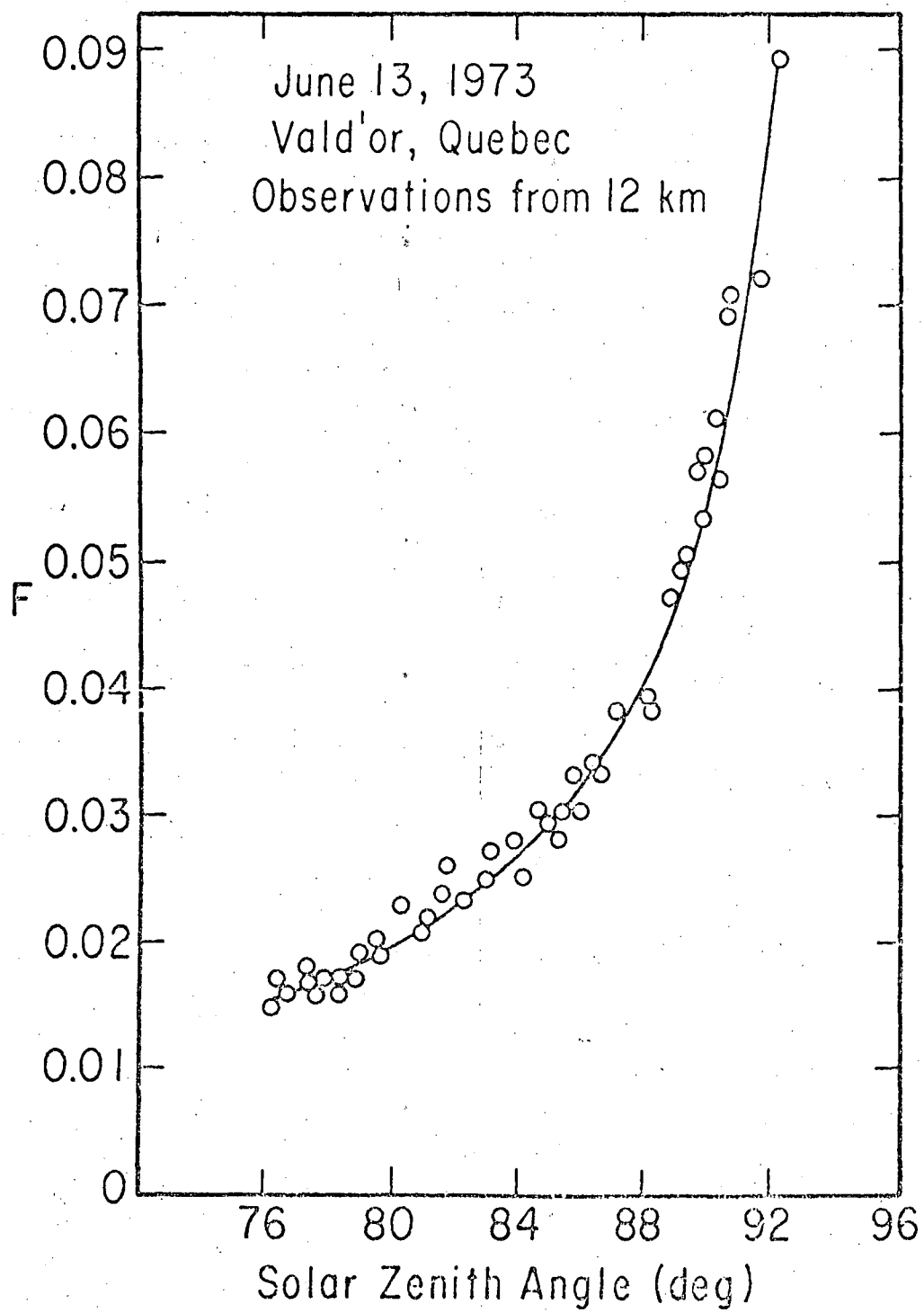


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Fig. 5

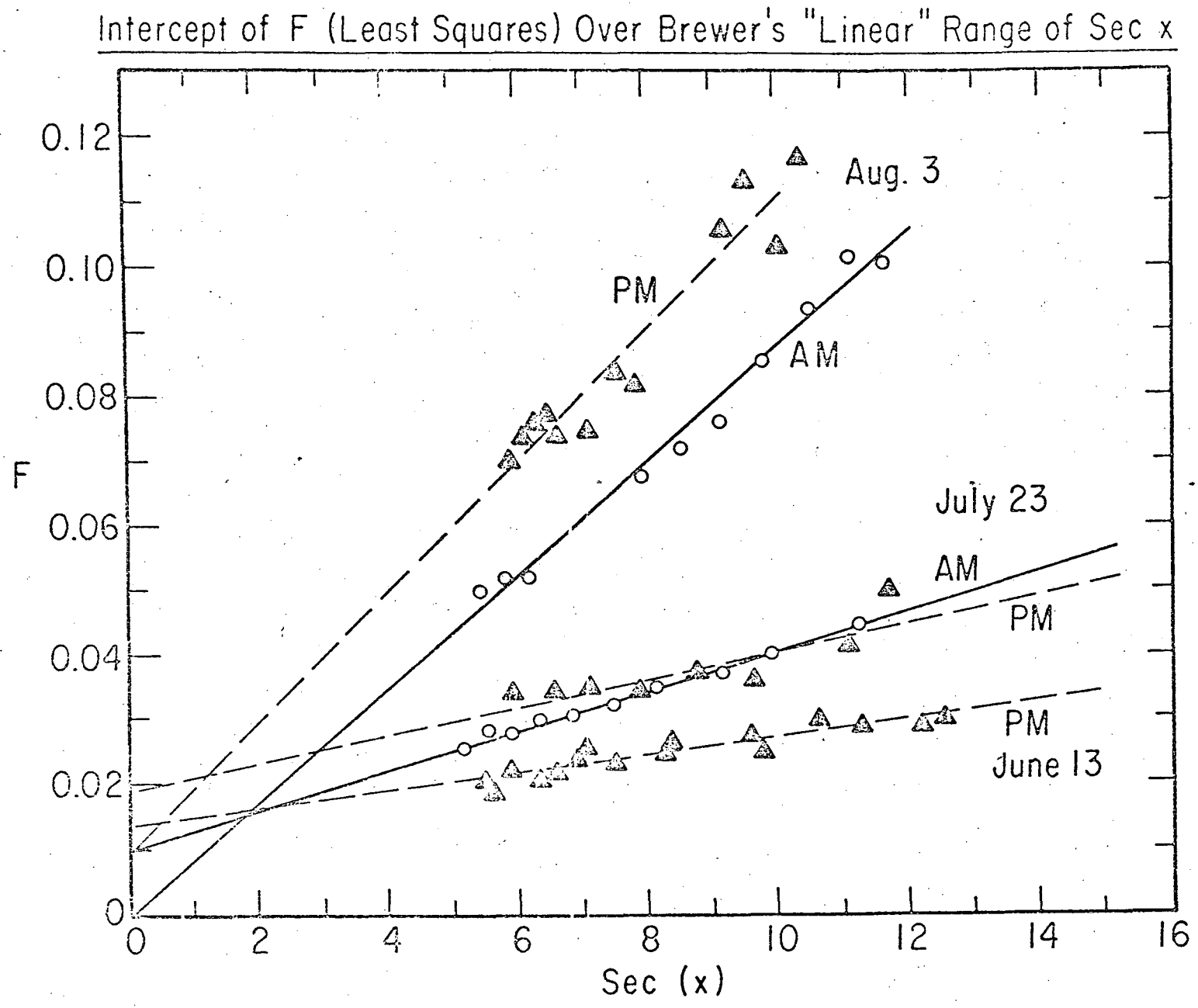


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Fig. 6

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0 0 0 0 4 1 0 4 Q21 6 0

Observed Brewer's F Function Extrapolated to $F_0$ in Two Ways (A, BC)

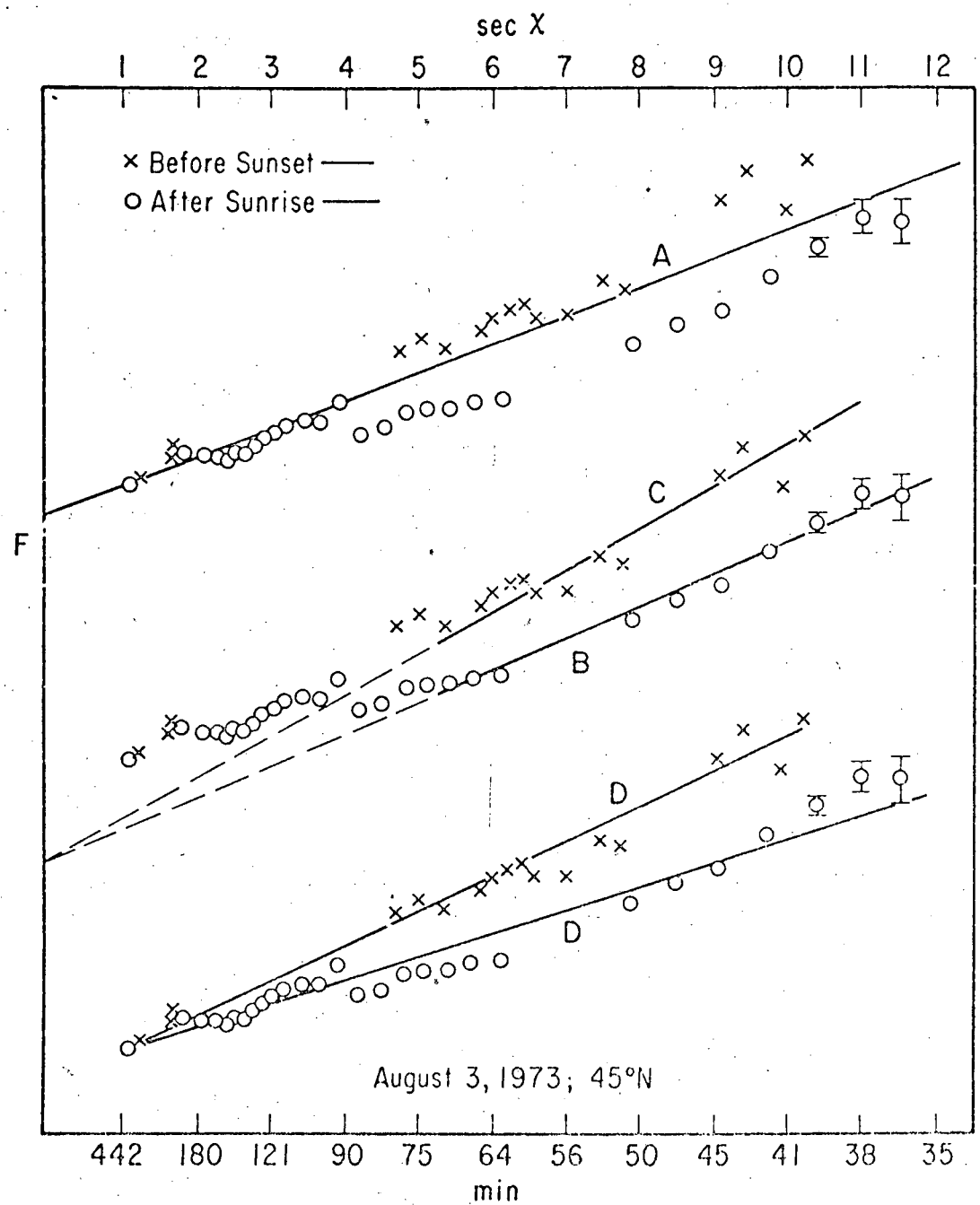


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Fig. 7

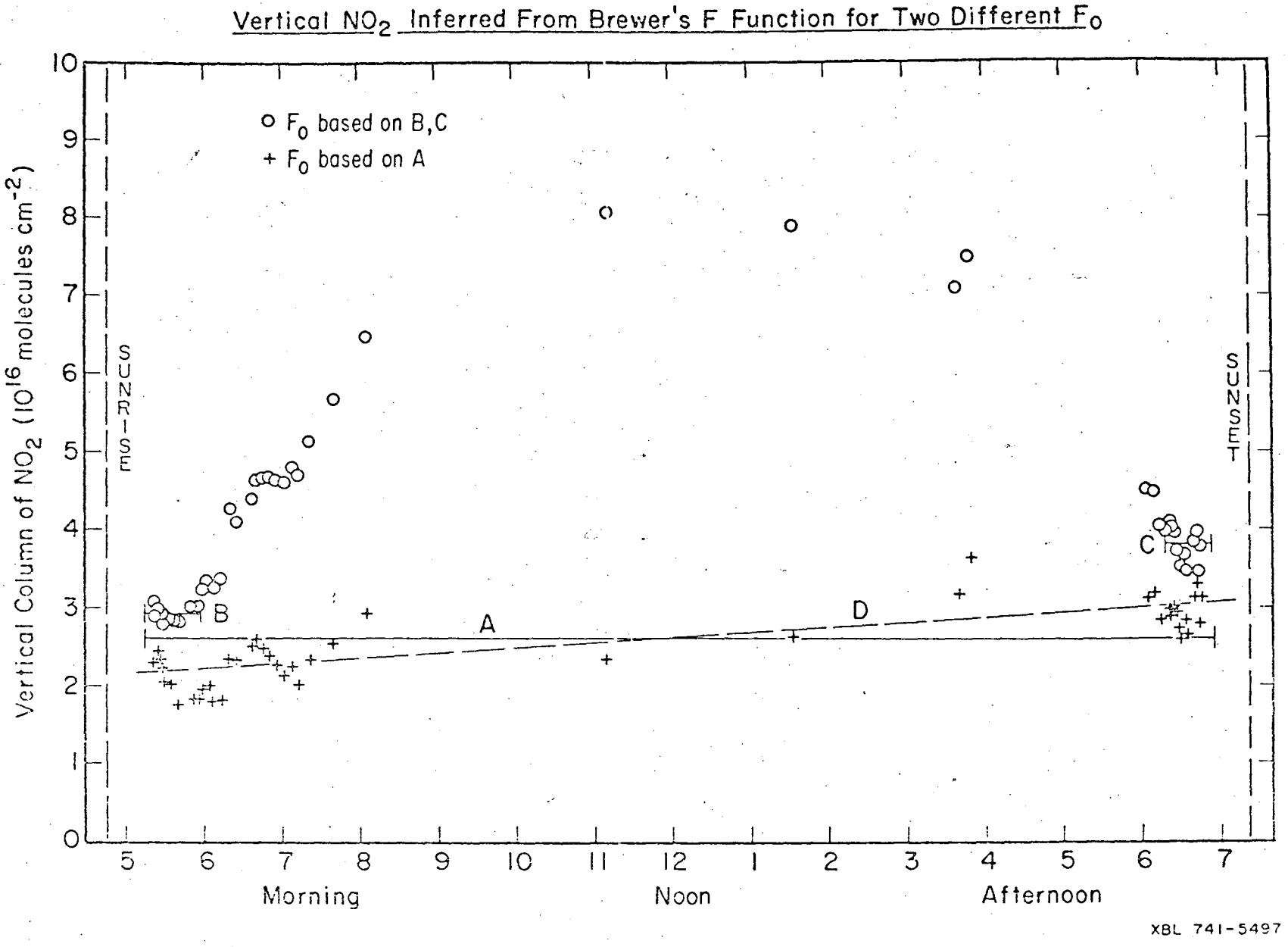
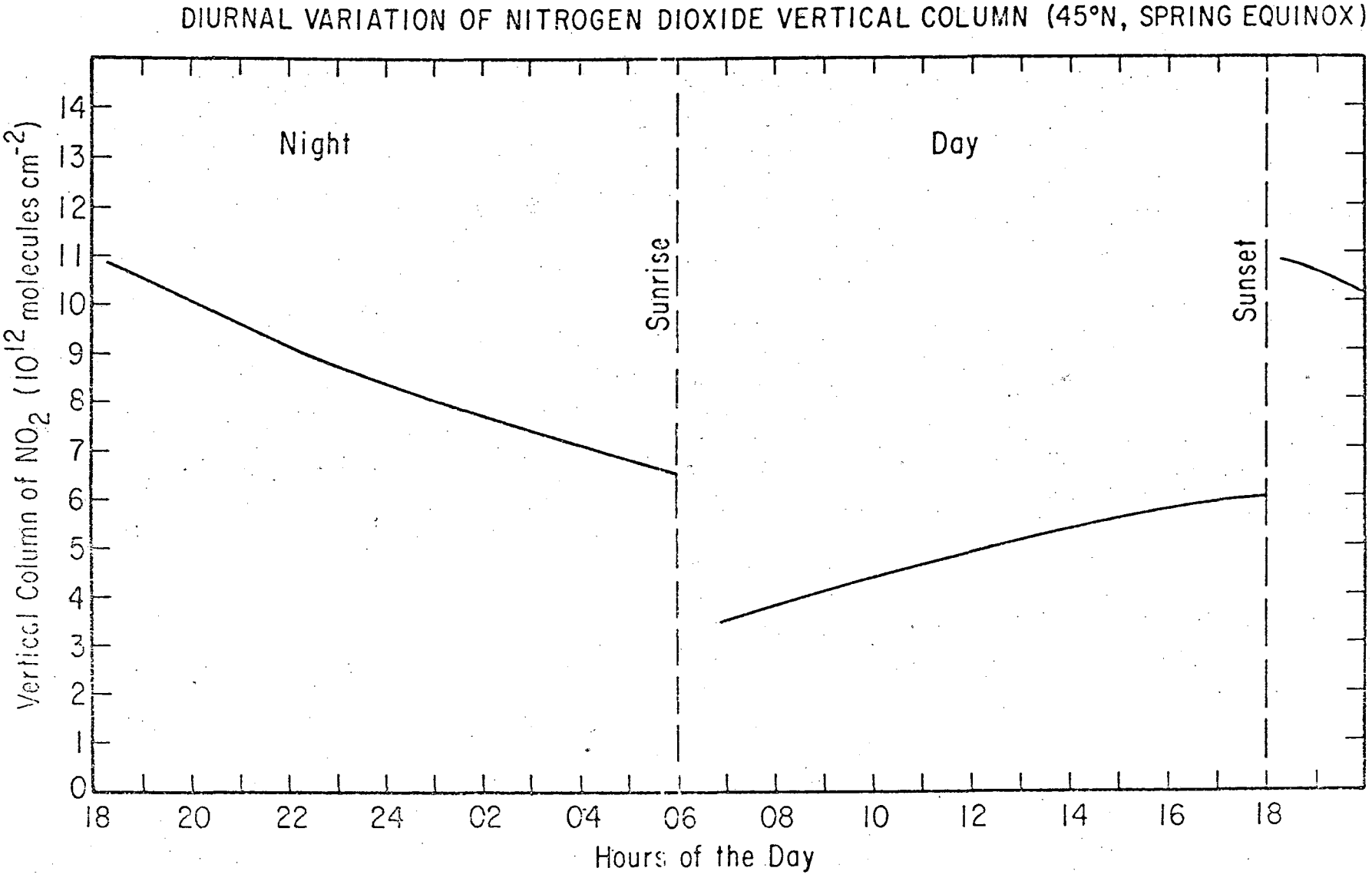

Vertical $NO_2$ Inferred From Brewer's F Function for Two Different $F_o$
Vertical Column of $NO_2$ ($10^{16}$ molecules $cm^{-2}$)
$F_o$ based on B,C
$F_o$ based on A
SUNRISE
SUNSET
A
B
C
D
Morning
Noon
Afternoon
XBL 741-5497

Fig. 8




XBL745-6273

Fig. 9

0 0 0 0 4 1 0 0 6 2
-23-

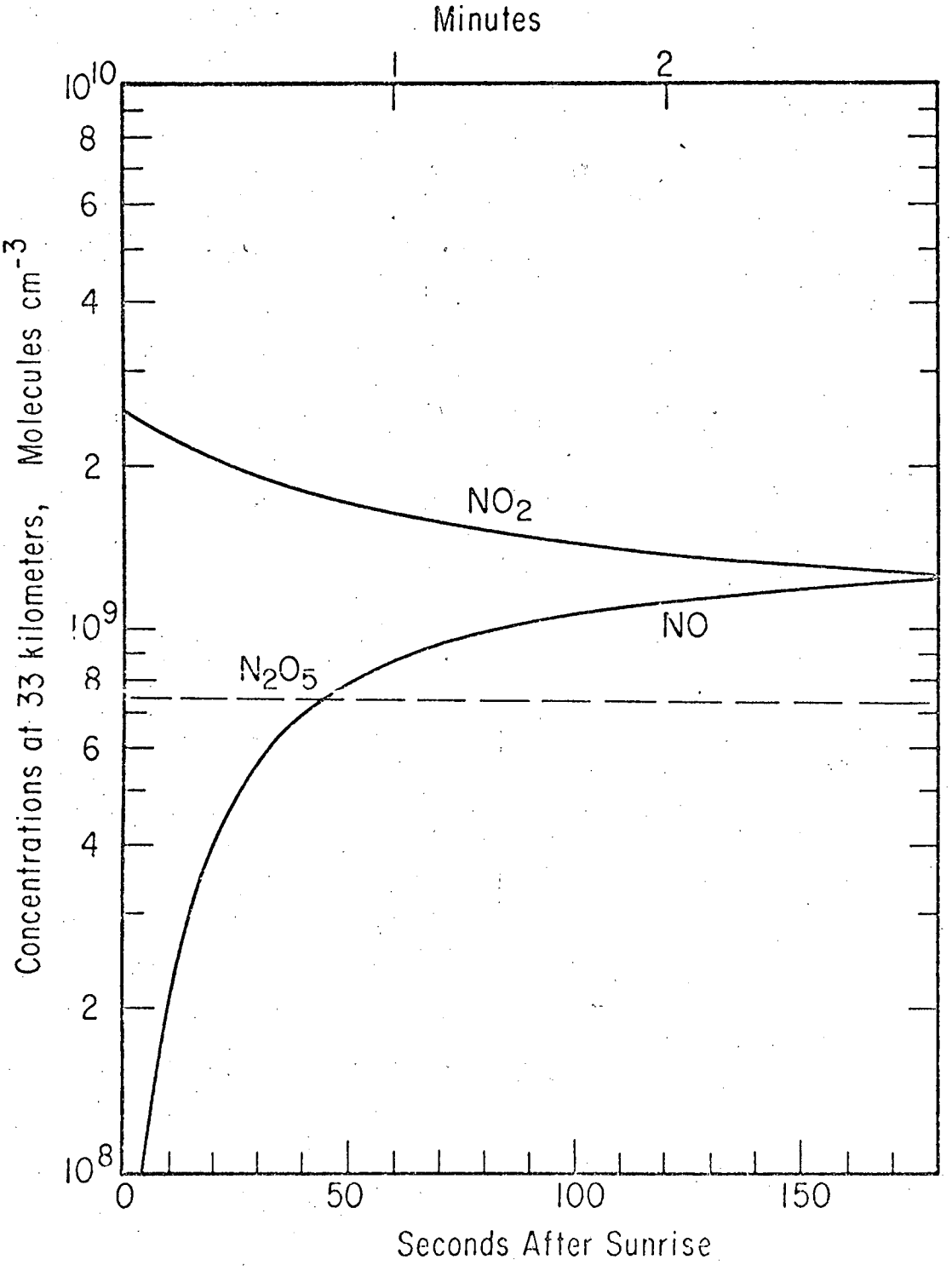



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Fig. 10

0 0 0 0 4 1 0 5 0 6 4

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