ACETONITRILE AND SULFURIC ACID CONCENTRATIONS DERIVED FROM ION COMPOSITION MEASUREMENTS DURING THE MAP/GLOBUS 1983 CAMPAIGN*

J. INGELS, D. NEVEJANS, P. FREDERICK and E. ARIJS

Belgian Institute for Space Aeronomy, Ringlaan 3, B-1180 Brussels, Belgium

Abstract—Acetonitrile volume mixing ratios are derived from positive ion spectra obtained with a balloon-borne quadrupole mass spectrometer in an altitude region from 21 to 32 km. Comparison of the results with data obtained in previous flights suggests a larger deviation from reference profiles, probably due to temporal transport phenomena.

From negative ion spectra obtained during the same balloon flight, the concentration of sulfuric acid vapour between 22 and 32 km is also deduced. These results seem to be in reasonable agreement with earlier data which were mostly obtained shortly after a period of enhanced volcanic activity.

1. INTRODUCTION

Since the first identification of stratospheric ions, realized with balloon-borne instruments in 1977 (Arijs *et al.*, 1978; Arnold *et al.*, 1978), considerable advance has been made in the field of balloon-borne ion mass spectrometry.

Whereas the first experiments were carried out at a single altitude, progress in ballooning technology has allowed an extension of the measurements in an altitude region from about 20 to 45 km. A simultaneous development of more sensitive, high resolution instruments also resulted in a more definite identification of positive and negative stratospheric ions and a determination of more detailed height profiles of the ion composition (for overviews of recent results, see Arnold, 1980, 1982; Ferguson and Arnold, 1981; Arijs, 1983; Arijs *et al.*, 1984).

The main findings are summarized hereafter. For positive ions, two major families were detected: the proton hydrates (PH) i.e. ions of the form $H^+(H_2O)_n$ and the so-called non proton hydrates (NPH) of the form $H^+(CH_3CN)_m(H_2O)_n$. A study of ion abundances based on steady-state considerations and explained hereafter, allowed the derivation of a mixing ratio profile of CH_3CN between 20 and 45 km. For negative ions, two major groups were found also; one consisting of clusters with NO_3^- as core ion and HNO_3 as a ligand and another with HSO_4^- as core ion and with HNO_3 and H_2SO_4 as ligands. A steady-state

method analogous to the one for positive ions resulted in the derivation of H_2SO_4 concentration profiles. This is an important result, as it provided the first estimations of the concentration of H_2SO_4, a trace gas important in aerosol formation processes.

Furthermore, it has been shown previously (Arnold *et al.*, 1980; Arijs *et al.*, 1981) that negative ion composition measurements may lead to an independent determination of HNO_3 mixing ratios in the atmosphere.

Originally, this was one of the main motivations to include stratospheric ion composition measurements in the MAP/GLOBUS 1983 campaign. Although this objective proved difficult to meet due to problems with cluster break-up (Arnold *et al.*, 1981a; Arijs *et al.*,1985), the ion mass spectrometer gondolas remained integrated in the MAP/GLOBUS 1983 campaign, because they can provide important information on other trace gases such as CH_3CN, a lon-glived species that may be useful as a tracer for transport problems, and H_2SO_4, the chemistry of which is closely related to aerosols, studied by other methods during this campaign (mainly by LIDAR).

2. EXPERIMENTAL METHODS AND MEASUREMENTS

The stratospheric ion spectra presented here were recorded over southern France on 18 September 1983 during our flight S-83 with gondola G7 of the MAP/GLOBUS 1983 campaign. A 100,000 m³ valve-controlled balloon, type 100 SF Zodiac, was launched at 13:11 U.T. from the CNES base near Aire-sur-l'Adour (approx. 44°N, 0°W), and a ceiling altitude

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of 32.2 km (7 mbar) was reached. Between 18:18 and 21:31 U.T., balloon and gondola descended at a rate of about 1.1 m s^{-1} from float altitude down to 20.0 km (52 mbar). The payload consisted of our quadrupole ion mass spectrometer QMS2 and an instrument to study aerosol properties by Earth limb photography (Ackerman et al., 1981). Total weight of the scientific instruments was 311 kg.

Our QMS2 instrument basically consists of a quadrupole mass filter and a Spiraltron detector (type Galileo Electro Optics secondary electron multiplier 4219) in a high speed liquid helium cryopump, and the appropriate electronic modules. Microprocessor-controlled operation guarantees a flexible system, allowing both positive and negative ion sampling with the same instrument. A detailed description of these parts is given elsewhere (Ingels et al., 1978; Arijs et al., 1980; Nevejans et al., 1982, 1985).

Stratospheric ions and neutral gases are sampled through a small hole of 0.25 mm diameter in a stainless steel flange of 0.1 mm thickness into a liquid helium cryopump. Behind the inlet hole, neutral gases are pumped and ions are focused into the quadrupole filter by an electrostatic lens, where the polarity of applied voltages is simply inverted between positive and negative ion modes. The high pumping speed of the cryopump (1,150 l s^{-1}) assures a pressure below 10^{-4} mbar throughout the altitude range covered. The sampling flange is insulated from and biased with respect to the gondola structure with a draw-in potential adjustable between -5 and $+5$ V. This draw-in potential is set for a maximum signal either by remote or by automatic control. After mass filtering, the ions reach the high gain spiraltron detector, signals of which are treated by pulse counting techniques. The cone of the spiraltron is kept at -3 and $+1.5$ kV for positive and negative ions respectively, resulting in an adequate detection efficiency. Mass range and sensitivity of the mass filter both depend upon resolution, determined by the ratios of DC and RF voltages applied to the quadrupole rods. In our instrument, resolution can be programmed by the on-board microprocessor. To record the present spectra, a moderate resolution mode ($M/\Delta M \approx 17$) was sufficient to resolve properly the major mass peaks and to determine the fractional abundances of the major ions in a mass range from 0 to 330 amu.

The spectra of stratospheric positive and negative ions discussed in this paper were recorded during the night-time, in the descent phase of the flight, to minimize contamination through gases desorbing from balloon and gondola (Arijs et al., 1983a). For the same reasons, the distance between balloon and gondola was kept at 170 m. Ambient pressure was measured in flight with a Baratron precision absolute capacitance manometer and temperature was recorded through use of beat thermistors mounted on an aluminium boom of about 1 m.

3. RESULTS AND DISCUSSION

3.1. Positive ions and acetonitrile mixing ratios

Although typical ion spectra obtained with our instruments were shown before (Arijs et al., 1982b, 1983a,b), it is worthwhile to give a typical positive ion spectrum as recorded in this flight in Fig. 1. In this figure, the presence of PH with mass numbers 55 and 73 is obvious, as well as that of NPH mass peaks. A list of observed mass numbers and their identification is given in Table 1.

All positive ion spectra of flight S-83 were obtained with the same moderate resolution ($M/\Delta M \approx 17$). Due to earlier high resolution data (Arijs et al., 1980) such a resolution still allowed identification of the major ions. It also permitted a determination of the ion abundances without having to correct for possible mass discrimination effects on the quadrupole transmittance.

The ion abundances derived from Fig. 1 are somewhat different from those of earlier spectra obtained at the same altitude. The most abundant NPH here is mass 78 in contrast to earlier data, where it was mass 96. This fact suggests a greater influence of cluster break-up effects in the present flight data, although sampling conditions (inlet hole diameter, draw-in potential, focus lens elements potentials) were very similar to those used in earlier flights.

It is, however, unlikely that these cluster break-up effects would result in conversion of NPH to PH, because the CH_3CN ligand is more strongly bound to the core ion than the H_2O ligand, due to its higher proton affinity. Therefore, the ion abundances can still be used to determine CH_3CN mixing ratios, $\mu(CH_3CN)$, as explained before (Arijs et al., 1983a)

TABLE 1. OBSERVED MAJOR POSITIVE IONS AND TENTATIVE IDENTIFICATION

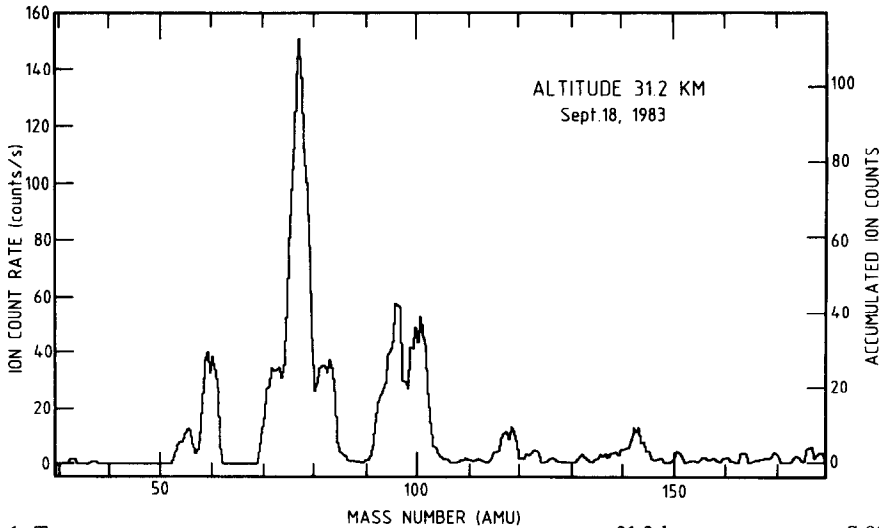| Mass number (amu)	Formula
55	$H^+(H_2O)_3$
60	$H^+(CH_3CN) H_2O$
73	$H^+(H_2O)_4$
78	$H^+(CH_3CN)(H_2O)_2$
83	$H^+(CH_3CN)_2$
96	$H^+(CH_3CN)(H_2O)_3$
101	$H^+(CH_3CN)_2 H_2O$
119	$H^+(CH_3CN)_2(H_2O)_2$
142	$H^+(CH_3CN)_3 H_2O$

FIG. 1. TYPICAL POSITIVE ION SPECTRUM OBTAINED AT AN ALTITUDE OF 31.2 km DURING FLIGHT S-83 OR
GONDOLA G7 OF THE MAP/GLOBUS 1983 CAMPAIGN.
The integration time for the accumulated counts is 0.75 s.

with a method based on the steady-state equation:

$$k_1 \mu(CH_3CN)[M][PH] = \alpha[n^-][NPH]. \qquad (1)$$

In this equation the symbols are:

k_1 = reaction rate constant for the conversion
    of PH to NPH in $cm^3 s^{-1}$,

[M] = total neutral atmospheric density in
    cm^{-3},

[PH] = total concentration of all PH ions in
    cm^{-3},

α = ion–ion recombination coefficient in
    $cm^3 s^{-1}$,

$[n^-]$ = total negative ion concentration in cm^{-3},

[NPH] = total concentration of NPH ions in cm^{-3}.

For calculating the mixing ratios of CH_3CN,
$\mu(CH_3CN)$, a value for k_1 of 3×10^{-9} $cm^3 s^{-1}$ as
reported by Smith et al. (1981) was used. The total
ion concentration $[n^-]$ was deduced from a para-
metrization of Heaps (1978) and for α the expression
(Arijs et al., 1983a)

$$\alpha = 6 \times 10^{-8} \left(\frac{300}{T}\right)^{1/2} + 1.25 \times 10^{-25} [M] \left(\frac{300}{T}\right)^4 \qquad (2)$$

was used, were T is the temperature in K. The mixing
ratios of CH_3CN can be calculated with formula (1)
if we assume that the height of a mass peak is pro-
portional to the corresponding ion abundance. The
results are represented by full circles labeled BISA in
Fig. 2 and the corresponding mixing ratios of CH_3CN
are given in Table 2. For the present data, [M] was

derived from a measurement of ambient pressure and
temperature, performed on the gondola.

The shaded area in Fig. 2 results from drawing an
envelope E for all extant measurements of $\mu(CH_3CN)$
apart from three extreme results and the data of this
MAP/GLOBUS 1983 campaign (Arnold et al., 1978,
1981c; Arijs et al., 1980, 1982b, 1983b; Henschen and
Arnold, 1981; Arnold and Henschen, 1982; Ingels
et al., 1986). A total of 106 mixing ratio values are
contained within this envelope E. The dotted line F
in Fig. 2 is obtained by fitting a second degree curve
through the 106 data points, so that

$$\log \mu(CH_3CN) = A + B \cdot z + C \cdot z^2 \qquad (3)$$

where z is the altitude in km. It is found that
$A = -28.01$, $B = 0.1678$ km^{-1}, and $C = -4.127 \times
10^{-3}$ km^{-2}. The standard deviation of the logarithm
of the data points from curve F is given by $S =
0.352$, which translates into a factor of 1.42 for
the mixing ratio itself. The full line M is the result
of a model calculation of CH_3CN (Arijs and Brasseur,
1986), adopting a global surface emission strength of
4.7×10^{10} g and assuming that acetonitrile is destroyed
mainly by reactions with OH and atomic oxygen. A
detailed discussion of this 1-D model is given by Arijs
and Brasseur (1986).

As can be seen from Fig. 2, the discrepancies
between the CH_3CN mixing ratios obtained during
our MAP/GLOBUS flight and the curves M and F
seem to be larger than those observed in previous
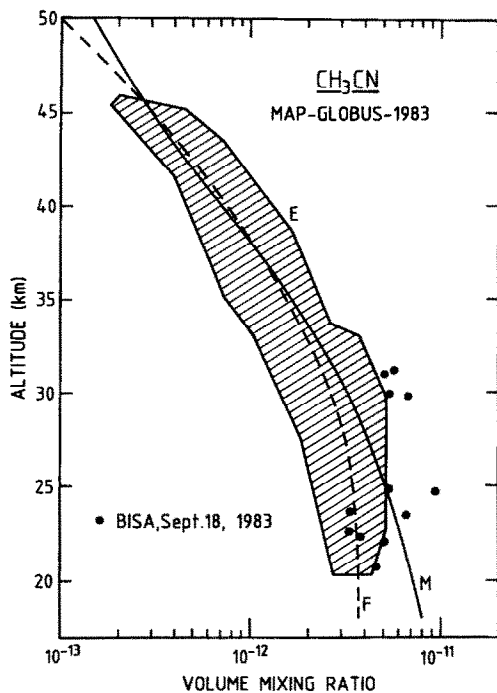flights. Most of the points actually fall out of the

FIG. 2. ACETONITRILE VOLUME MIXING RATIOS AS OBTAINED IN THE MAP/GLOBUS 1983 CAMPAIGN COMPARED TO PREVIOUS MEASUREMENTS (SHADED AREA E) AND A MODEL CALCULATION (M).
The dotted line F represents a fitting through earlier data points.

TABLE 2. ACETONITRILE MIXING RATIOS AS INFERRED FROM POSITIVE ION SPECTRA IN THE S-83 FLIGHT

Altitude (km)	Mixing ratio ($\times 10^{12}$)
31.2	5.5
31.0	5.0
30.0	5.4
29.8	6.6
25.0	5.2
24.7	9.5
23.7	3.4
23.5	6.8
22.6	3.3
22.4	3.8
22.1	5.0
20.8	4.7

envelope E of all previous measurements. It is clear therefore that the CH_3CN profile observed in this flight is deviating to a larger extent from an expected mean profile than the earlier data. Similar deviations have been observed in this campaign in the mixing ratio profiles of other trace gases and are discussed to a larger extent in a separate paper by Offermann et al. (1987).

In order to compare the deviations with those measured during the MAP/GLOBUS 1983 campaign derived for other trace gases such as O_3, HNO_3, H_2O, N_2O, CH_4 and CF_2Cl_2, we have presented them in the same way, i.e. the quotient of the mixing ratios as derived from the ion mass spectra and those given by a reference profile are shown as a function of altitude in Fig. 3. However, in making a comparison, some important points need to be kept in mind.

(1) The choice of a reference profile for CH_3CN is not straightforward. Curve F (a fit to previous experimental data) is only representative for a limited number of data, all obtained by the same technique and in a limited altitude range (20–45 km), where the data above 40 km only result from one balloon flight. In addition, the choice of curve M (a model calculation) is somewhat arbitrary, since it was shown (Arijs and Brasseur, 1986; Ingels et al., 1986) that different model profiles agreeing reasonably with experimental results can be obtained, depending upon the use of the CH_3CN emission strength, reaction rates and eddy diffusion coefficients used in the model calculations. We have adopted here a model result giving the best agreement with experimental CH_3CN mixing ratios between 20 and 45 km and resulting in ion distributions consistent with experimentally obtained ones (Ingels et al., 1986).

In view of the difficulty in choosing a so-called reference profile, the deviations from both curves M and F are displayed in Fig. 3. Also shown in Fig. 3 are the limits for the deviations given by one and two standard deviations from the fitting F, labeled S and 2S, respectively.

(2) The experimental uncertainties on CH_3CN mixing ratios derived from flight S-83 are estimated to be of the order of 20–30% above 25 km and to be somewhat larger below this altitude due to less complete counting statistics in the low altitude spectra. This uncertainty, however, does not take into account possible errors on the values of k_1, α and $[n^-]$ used here.

Nevertheless, the deviations from the "standard" profiles around 30 km as shown in Fig. 3 are larger than those observed for earlier flights and they seem to suggest the presence of a larger disturbance in the stratosphere. Below 25 km, the S-83 data show a considerable amount of scatter and it is difficult to be conclusive about the deviations, especially in view of the dilemma in choosing the exact reference profile (M or F). Disturbances giving rise to temporal variances (or deviations from standard profiles) can be ascribed to dynamics or transport phenomena (Ehhalt et al., 1983). The present set of data on its own, however, does not allow one to speculate on the nature
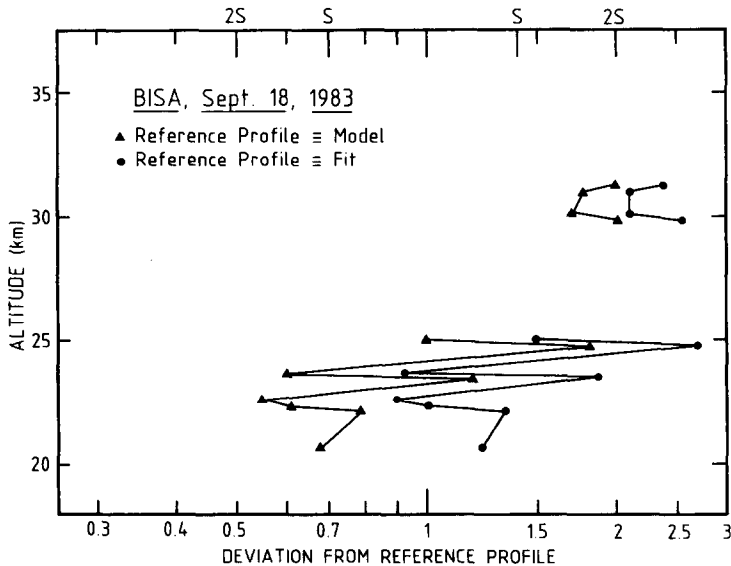
FIG. 3. DEVIATION OF PRESENT CH₃CN VOLUME MIXING RATIOS FROM REFERENCE PROFILES F AND M
EXPRESSED AS QUOTIENTS OF THE ACTUAL DATA AND REFERENCE VALUES.
S and 2S are one and two standard deviations from the fitting F (for details see text).

of the dynamical processes (waves, tides, or other) involved here. A more detailed analysis of all profiles obtained for other trace gases in this MAP/GLOBUS 1983 campaign is needed to do so. It should be noted, however, that CH_3CN is a good trace gas to use in such an analysis, in view of the long lifetime of this molecule (0.5–1.4 y; Arijs and Brasseur, 1986).

3.2. Negative ions and sulfuric acid concentrations

During a considerable part of the descent from float altitude down to 22 km, measurements were performed in the negative ion mode. Typical spectra as well as a more detailed discussion of the negative ion composition data of flight S-83 have already been given elsewhere (Arijs et al., 1985). The observed major ions were $NO_3^-(HNO_3)_n$ and HSO_4^- $(H_2SO_4)_l(HNO_3)_m$ clusters, indicated hereafter by n_N^- and n_S^-, respectively. Due to the fact that conversion of n_N^- to n_S^- ions proceeds through a reaction with sulfuric acid vapor

$$n_N^- + H_2SO_4 \rightarrow n_S^- + HNO_3 \qquad (4)$$
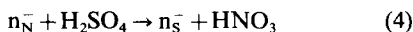
with a reaction rate coefficient k_2 measured in the laboratory (Viggiano et al., 1980, 1982), the spectra allow a derivation of the H_2SO_4 number density through the steady-state equation

$$k_2[H_2SO_4 + HSO_j][n_N^-] = \alpha[n_S^-][n^+] \qquad (5)$$

where square brackets stand for number densities and $[n^+]$ is the total positive ion density. The term HSO_y in

equation (5) represents possible other sulfur-bearing gases also leading to conversion of n_N^- to n_S^- clusters. It has been suggested that these gases mainly consist of HSO_3 (Arnold et al., 1982; Qiu and Arnold, 1984), which is an intermediate product in the formation of H_2SO_4, produced by the reaction

$$SO_2 + OH + M \rightarrow HSO_3 + M. \qquad (6)$$

Recently, however, it was suggested by Stockwell and Calvert (1983) that further conversion of HSO_3 proceeds through

$$HSO_3 + O_2 \rightarrow HO_2 + SO_3. \qquad (7)$$
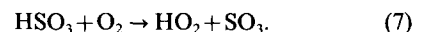
If, however, this reaction is the major loss process for HSO_3, then the presence of HSO_3 in measurable quantities in the stratosphere would become very doubtful, as was indicated before (Arijs et al., 1985). Recent laboratory measurements by Margitan (1984) showed that the rate constant for reaction (7) was $(4 \pm 2) \times 10^{-13}$ cm³ s⁻¹, allowing one to conclude that the presence of HSO_3 in the stratosphere is very unlikely. Therefore we believe that the $H_2SO_4 + HSO_y$ number density derived from equation (4) mainly consists of $[H_2SO_4]$.

The H_2SO_4 number densities as derived from flight S-83 are shown in Fig. 4. The shaded area in this figure corresponds to the envelope of all previous data (Arijs et al., 1982a, 1983c,d, 1985; Arnold and Fabian, 1980; Arnold et al., 1981b; Arnold and Bührke, 1983; Arnold and Qiu, 1984; Qiu and Arnold, 1984); the
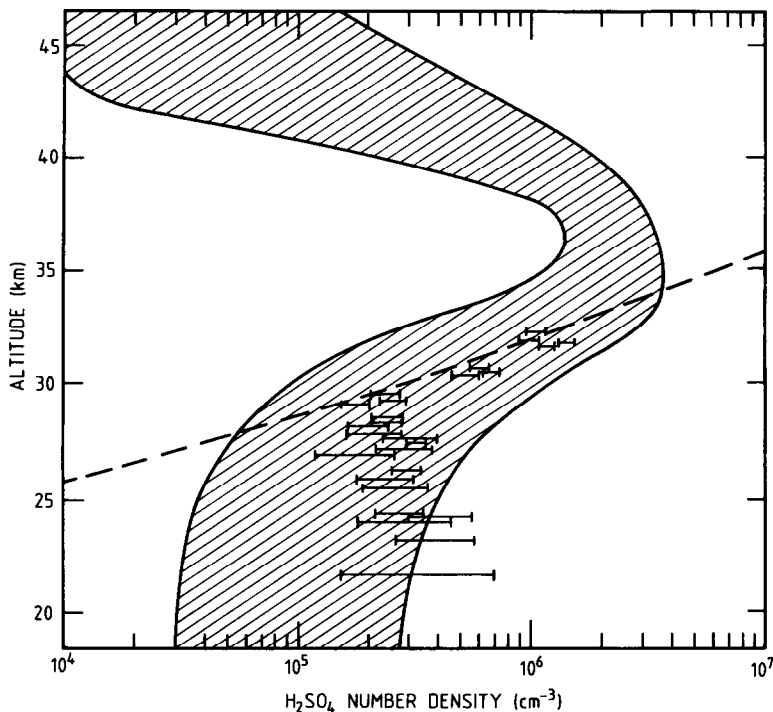
FIG. 4. SULFURIC ACID CONCENTRATIONS DERIVED FROM NEGATIVE ION COMPOSITION DATA OBTAINED IN THE MAP/GLOBUS 1983 CAMPAIGN COMPARED TO EARLIER DATA (SHADED AREA) AND A VAPOR PRESSURE CALCULATION (DOTTED LINE).
Error bars are due to uncertainties in ion abundance measurements and not to uncertainties in kinetic data.

dotted line represents a vapor pressure calculation by a procedure explained elsewhere (Arijs *et al.*, 1983c). Although calculations of the vapor pressure were made assuming a flat surface of a $H_2SO_4-H_2O$ mixture, it can easily be shown that the results will differ only by a few percent using spherical surfaces with a radius of the order of 0.05–0.1 μm, i.e. the typical dimensions of stratospheric aerosols.

Taking into account the error bars, the data fall reasonably well within the envelope of the previous results, and no marked deviations due to transport effects, as suggested by the data of CH_3CN, are noticed around 30 km. It is tempting to conclude that the larger supersaturation of the inferred H_2SO_4 concentration below about 25 km altitude compared with the mean value of the previous results also reflects interaction of dynamical processes. This conclusion, however, is rather speculative because of the large uncertainties on the H_2SO_4 concentrations due to the low count rate observed in the negative ion spectra obtained below 25 km. It should also be kept in mind that most of the earlier data about H_2SO_4 were obtained during the period from June until October

1982 after the eruption of the volcano El Chichon (4 April 1982). This eruption resulted in a disturbed stratospheric sulfur chemistry due to injections of large supplementary quantities of SO_2 and other sulfur-bearing gases. It is therefore very difficult to derive an average H_2SO_4 profile from the previous data and an analysis similar to the one for CH_3CN would probably not be representative.

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