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SULFURIC ACID VAPOUR DERIVATIONS FROM NEGATIVE ION COMPOSITION DATA BETWEEN 25 AND 34 KM

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Abstract : Negative ion composition measurements obtained during a valve controlled balloon flight were used to derive (H_2SO_4 + HSO_y) number densities between 25 and 34 km altitude. The data are compared to similar results obtained for other stratospheric temperatures. The implications of the results on our present ideas about aerosol formation are briefly discussed.

Introduction

Although H_2SO_4 plays a key role in the formation of aerosols (Turco et al., 1982), measurements of its concentration in the stratosphere have not been possible until very recently. Stratospheric negative ion composition measurements (Arnold and Henschen, 1978; Arijs et al., 1981) have shown the existence of HSO_4^- cluster ions formed through switching reactions between H_2SO_4 and NO_3^- cluster ions. Subsequent laboratory studies (Viggiano et al., 1980) revealed the rate constants of these reactions and made it possible to deduce sulfuric acid concentrations in the stratosphere (Arnold and Fabian, 1980). The technique explained briefly hereafter, has been exploited extensively by Arnold and coworkers (Arnold et al., 1981; Viggiano and Arnold, 1981; Viggiano and Arnold, 1983).

Most data published so far were obtained during autumn. In the present paper we report some recent measurements performed during summer conditions and briefly discuss the implication on the present ideas about aerosol formation.

Experimental and measurements

The data shown and discussed hereafter were obtained during a flight performed with a valve controlled balloon on 16 June 1982 from the CNES launching base at Gap-Tallard (S. France). The balloon borne ion mass spectrometer has been described in detail before (Arijs et al., 1980; Ingels et al., 1978; Nevejans et al., 1983).

The mass range of the spectrometer is limited to 330 amu in the high resolution mode, but use of low resolutions allows detection of ions with masses larger than 330 amu.

For the negative ion measurements two resolution modes have been used. At float altitude spectra were obtained in a moderate resolution mode ($m/\Delta m \cong 17$), adequate to resolve the major ions. During descent, series of multiple scans with moderate resolution were recorded alternated with single scans in the total ion mode (no DC on the quadrupole rods). In this way spectra were obtained from 34 km down to 25 km altitude, either at float altitude or during the descending phase of the balloon flight.

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Results and discussion

Two typical spectra obtained in the moderate resolution mode are shown in figure 1. As observed, the amplitudes of the mass peaks due to $HSO_4^-(HNO_3)_m(H_2SO_4)_\ell$ ions (mass numbers 160, 195 and 293) decrease with decreasing altitude, which illustrates the variation of sulfuric acid number density with altitude.

As pointed out by Arnold and Fabian (1980) the sulfuric acid number density $[H_2SO_4]$ can be deduced through the formula :

$$k[n_N^-]\ [H_2SO_4] = \alpha[n^+]\ [n_S^-] \quad (1)$$

where $[n^+]$ is the total positive ion number density, α the ion-ion recombination coefficient, k the reaction rate coefficient for switching reactions between NO_3^- cluster ions and sulfuric acid, $[n_S^-]$ the sum of the number densities of all HSO_4^- cluster ions and $[n_N^-]$ the total density of all ions with a NO_3^- core. The values of k and α are assumed to be the same for all ion-molecule and ion-ion reactions.

Recently it was discovered (Arnold et al., 1982) that other sulfur bearing gases may contribute to the formation of HSO_4^- cluster ions. Therefore formula (1) should be replaced by :

$$k[n_N^-]\ ([H_2SO_4] + [HSO_y]) = \alpha[n^+]\ [n_S^-] \quad (2)$$

where HSO_y includes HSO_3 and HSO_5 and any other sulfur compound that can react with NO_3^- cluster ions to form HSO_4^- cluster ions.

The calculation of the ion abundances $[n_N^-]$ and $[n_S^-]$ to be used in formula (2) is straightforward. From spectra as those shown in figure 1, the ion abundances are derived assuming that ion count rates reflect ion number densities. This sounds reasonable in view of the moderate resolution used, which yields small mass discrimination. The results are not affected by cluster break-up since $[n_S^-]$ and $[n_N^-]$ are the number densities of all ions with HSO_4^- cores and NO_3^- cores respectively and collisional induced dissociation does not modify the core of the cluster ions. Due to the limited mass range of the mass filter (330 amu) it may be expected that some ions will not be detected. This is especially true at altitudes above 30 km where mass 391, i.e. $HSO_4^-(H_2SO_4)_3$, represents a considerable fraction of the total ion signal (Arijs et al., 1981). In order to calculate the signal due to missing ions, the spectra obtained in the total ion mode were used, assuming that all ions with masses larger than 330 amu are due to HSO_4^- cluster ions, as confirmed by previous measurements (Arijs et al., 1981; Arnold et al., 1982).

For the ion-ion recombination coefficient α, recent data based on in-situ measurements (Rosen and Hofmann, 1981), laboratory work (Smith and Adams, 1982) and theoretical calculations (Bates, 1982) are available. In order to compromize

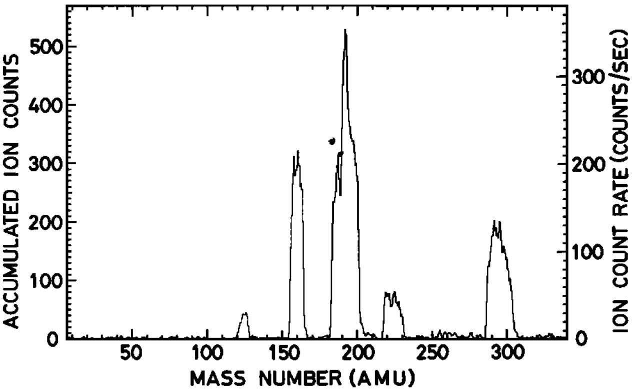

Fig. 1a. Typical negative ion spectrum in the moderate resolution mode obtained at 32 km after summation of 6 scans of 160 s each.

between these different data we have used a parametrization of the form :

$$\alpha = 6\mathrm{x}10^{-8}\ (300/T)^{0.5} + 1.25\mathrm{x}10^{-25}\ [M](300/T)^{4} \quad (3)$$

where T is temperature in Kelvin, [M] total gas number density in cm^{-3} and α is in $cm^3\ s^{-1}$.

This parametrization gives α values, representing an average of the data in the literature referred to above, between 30 and 20 km altitude. Above 30 km the value given by formula (3) is in better agreement with the recent data of Bates (1982). Using the extreme values of α as reported in the cited references (Smith and Adams, 1982; Bates, 1982) results in a difference of a factor of 1.5 in the derived $[H_2SO_4 + HSO_y]$ values.

The total positive ion density is deduced from the continuity equation $[n^+] = (Q/\alpha)^{1/2}$, where the ion pair production rate Q is calculated with the parametrization of Heaps (1978).

For the reaction rate coefficient k, the recently corrected values, published by Viggiano et al. (1982) were used. A value of 1.1 x 10^{-9} $cm^3\ s^{-1}$ was reported for the reaction of H_2SO_4 with $NO_3^-(HNO_3)_2$ and since the latter was the most abundant ion with NO_3^- core in our spectra, only this value will be applied in formula (2).

The $(H_2SO_4 + HSO_y)$ number densities obtained from the negative ion spectra at different altitudes are shown in figure 2, together with a compilation of data previously obtained by our group and by the group of the Max Planck Institut of Heidelberg (MPIH hereafter) (Viggiano and Arnold, 1983). In view of the uncertainties on k and α, the errors on the $[H_2SO_4 + HSO_y]$ values are estimated to be a factor of 3. The data are also compared with different model calculations.

The numbered curves are H_2SO_4 vapour pressure calculations performed by us assuming that the water vapour mixing ratio in the stratosphere is constant and that the aerosols consisted of liquid droplets of a homogeneous water/sulfuric acid mixture. Following Hamill et al. (1977) we accepted that the water vapour is in equilibrium with the H_2SO_4-H_2O droplets. Using the vapour pressure data of Gmitro and Vermeulen (1964), which seem to be only reliable for water vapour pressure calculations (Verhoff and Banchero, 1972) the weight percentage of H_2SO_4 in the aerosols at different altitudes (or different temperatures) was calculated. From this and the temperature, the partial vapour pressure of sulfuric acid was derived with the formula reported by Ayers et al. (1980). Curves 1 and 2 represent the results of such a computation for a 3 ppm water mixing ratio and a U.S Standard Atmosphere temperature profile, for spring-fall and summer conditions respectively.

As was noted by Viggiano and Arnold (1983) there is good agreement between curve 1 and the MPIH data in the altitude region 35 to 28 km. If a constant water vapour mixing ratio of 1.5 ppm is accepted, this agreement is even excellent (curve 1A). This however is probably fortuituous, regarding the low H_2O mixing ratio (1.5 ppm), the large uncertainties on the thermochemical data used to calculate the H_2SO_4 vapour pressure (Verhoff and Banchero, 1972; Ayers et al., 1980) and the errors on the deduced H_2SO_4 number densities. As can be seen the agreement between our data and curve 2 is rather poor. In order to investigate this, we have plotted the temperature versus time as measured by a tiny bead thermistor during the ascent period of the flight. This measurement took place at night so that errors introduced by solar radiation are insignificant.

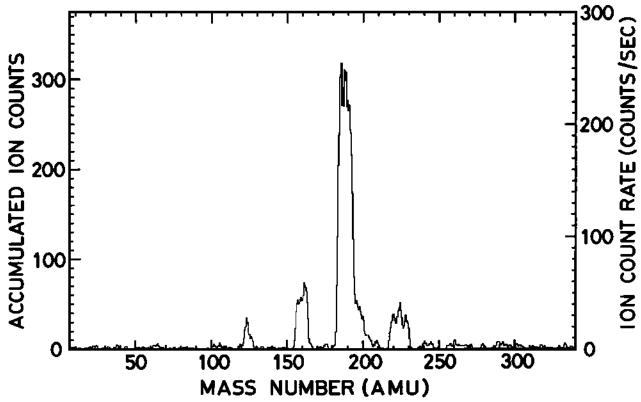

Fig. 1b. Moderate resolution negative ion spectrum obtained at 28 km after summation of 5 scans.
Both spectra were smoothed as described before (Arijs et al., 1982).

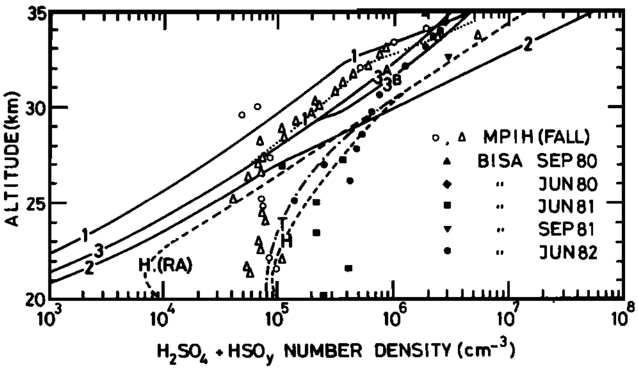

Fig. 2. $[H_2SO_4 + HSO_y]$ obtained in-situ by different experiments compared to vapour pressure calculation and recent models. Curve T refers to the work of Turco et al. (1981), H are model calculations of Hamill et al. (1982), R.A. representing the radical agglomeration case.

The result is represented by curve 1 in figure 3. For comparison U.S. Standard Atmosphere temperatures at the same altitudes are represented by curve 2 and 3 for summer and spring-fall conditions respectively. Strong fluctuations probably related to balloon motions, occur on the observed temperature, especially at ceiling altitude. Nevertheless it can be concluded that the measured temperature is closer to the spring-fall profile after 0.30 UT, which corresponds to about 30 km. For the derivation of the H_2SO_4 vapour pressure we have therefore adopted two tentative temperature profiles, which fit better to the measured one. Using a simple linear relation $T = 195.2 + 1.15\ z$, where z is the altitude in km, results in curve 3A of figure 2. Taking the same relationship for $z \leq 28$ and $T = 185 + 1.5\ z$ for higher altitudes, results in curve 3B.

The agreement between experimental data and the H_2SO_4 vapour pressures now obtained is within the experimental errors down to about 28 km.

According to model calculations (Turco et al., 1979) the concentration of H_2SO_4 is much larger than that of HSO_3 above 28 km. It is therefore reasonable to conclude that above this altitude the major compound detected by the present technique is H_2SO_4. The agreement of our data with our calculated values of sulfuric acid vapour therefore suggests that the H_2SO_4 number density above 28 km is mainly controlled by evaporation from aerosols. This confirms the present ideas about aerosol formation and the measurement of Viggiano and Arnold (1983) who drew the same conclusion.

Below 28 km the data values are much higher than the vapour pressure values, indicating supersaturation leading to aerosol growth.

It is tempting to compare the data to the models of Turco and Hamill shown in figure 2. This however is premature since the measured concentrations are referring to H_2SO_4 plus all other sulfur compounds which can give rise to HSO_4^- ions. These include HSO_3, the concentration of which can exceed the H_2SO_4 concentration below 28 km (Turco et al., 1981). Therefore a comparison should be made with the total concentration of all sulfur compounds resulting in HSO_4^- clusters. Unfortunately no recent models giving this quantity as a function of altitude and temperature are available yet.

It is evident however from figure 2 that $(H_2SO_4 + HSO_y)$ concentrations are found which are considerably higher than in the experiments of Viggiano and Arnold (1983). At present however it is difficult to conclude whether this is due to higher stratospheric temperatures, or to recent volcanic eruptions (El Chichón, April 1982). The latter might have increased considerably the amount of SO_2 in the stratosphere and consequently the resulting formation of H_2SO_4 and HSO_y. It should be noted that all our data were obtained during descent, so that contamination effects cannot be responsible for our higher values. Furthermore this difference is not due to the use of a value of the ion-ion recombination coefficient α and the ion production rate Q, being different from those used by the referred authors. On the contrary even higher $(H_2SO_4 + HSO_y)$ concentrations are found with their α and Q values and our ion abundances.

It should also be noted that the errors on our

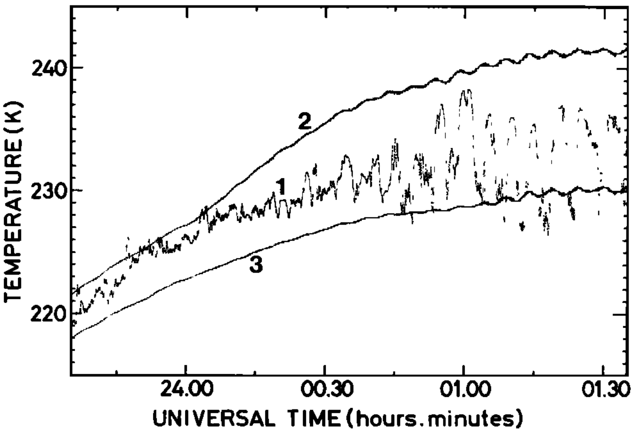

Fig. 3. Temperature versus time during ascent in the balloon flight of 16 June 1982.
Curve 1 : temperature as measured; 2: U.S. Standard Atmosphere temperature for summer conditions, derived from the conversion of pressure measurement to altitude; 3: same for spring-fall.

1981 data are somewhat larger, due to the lower resolution used (Arijs et al., 1982).

It is clear that more measurements at different stratospheric temperatures are required to elucidate the problem.

Conclusive remarks

A comparison of sulfuric acid vapour pressure calculations with the data set on $(H_2SO_4 + HSO_y)$ concentrations between 28 and 35 km altitude seems to support the present ideas about the interaction of H_2SO_4 with aerosols.

It should be noted however that this interpretation is relying on information, still suffering from some inaccuracies due to different experimental factors which need further investigations. Among those we cite the errors on the sulfuric acid vapour pressure calculations due to the uncertain values of the thermodynamic quantities involved (Verhoff and Banchero, 1972).

As noticed from figure 2 small changes in temperature and water mixing ratios have a considerable effect on the sulfuric acid partial pressure. A precise measurement of both water mixing ratio and temperature is therefore needed. Also the influence of other substances, such as impurities or possibly HNO_3 dissolved in aerosols (Kiang and Hamill, 1974) should be investigated.

Below 28 km the interpretation of the data is hampered by the fact that the present technique cannot distinguish between H_2SO_4 and other sulfur compounds which may lead to HSO_4^- cluster ions. Laboratory measurements of the ion-molecule reactions of HSO_3, HSO_5 and other sulfur compounds with NO_3^- cluster ions may help to assess their role. Furthermore model calculations of these sulfur compounds would be very helpful.

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