Chemical Events in the Atmosphere and their Impact on Environment
Pontifical Academy of Sciences, *Scripta Varia* 56, Vatican City 1985
www.pas.va/content/dam/accademia/pdf/sv56/sv56-arnold.pdf

ATMOSPHERIC IONS

F. ARNOLD
Max-Planck-Institut für Kernphysik
6900 Heidelberg, Postfach 103980 - F.R. Germany

ABSTRACT

Considerable progress has been made during recent years in exploring the ionized component of the denser regions of the earth's atmosphere, the stratosphere, and troposphere. It has been found that in these regions the plasma is composed mostly of large positive and negative cluster ions formed via a complex network of ion-molecule reactions starting from simple atomic and molecular primary ions. Various neutral trace gases involved as reactants in these ion transformations can be detected by measuring the ion composition. During recent years, this analytical application of in situ ion composition measurements became a powerful tool for trace gas detection and perhaps represents the most important aspect of current atmospheric ion research. The present paper reviews our present understanding of atmospheric ions with an emphasis on recent progress in stratospheric and tropospheric ion research. Interest will also be focussed on analytical applications and ion-induced aerosol formation.

INTRODUCTION

Atmospheric gaseous ions not only control the electrical properties of the atmospheric medium but also have an interesting role in atmospheric chemistry. They have the potential to stimulate the formation of aerosols by ion-induced nucleation [1, 4] and to form or destroy trace gases by ion-molecule or ion-catalyzed reactions. Apart from these active roles ions also have an interesting passive role in serving as powerful probes for trace gases and aerosols coexisting with the ions in the atmospheric medium [1]. This analytical application, which was introduced only during recent years, perhaps represents the most important aspect of current atmospheric ion research. It has already provided a wealth of interesting and new information on various atmospheric trace gases [1] also including species which could not be detected previously by other means than for example sulfuric acid vapour [2-10] which is of considerable importance since this trace gas has a key role in atmospheric aerosol formation. The ultimate physical cause of the importance of atmospheric ions lies in their very efficient interaction with atmospheric atoms, molecules, ions, and electrons. This interaction, of course, is due to long-range charge-dipole and Coulomb attraction forces which give rise to large collision cross sections, increase chemical reactivity, and promote the formation of molecular clusters by electrostatic bonding.

Our current understanding of the chemical nature of atmospheric ions and their role in atmospheric aerosol and trace gas processes derives primarily from in situ ion composition measurements using rocket-, balloon-, and aircraft-borne mass spectrometers [11, 12] as well as from laboratory studies of ion-molecule reactions and ion nucleation [13, 14].

Atmospheric plasma research was originally stimulated by the interest in radio wave propagation and therefore was focussed on the ionosphere. Thus, the early in situ ion composition measurements were made in the ionosphere at altitudes above about 100 km using rocket-borne spectrometers [15, 16, 17]. Below 100 km, the atmospheric gas pressure becomes so large that mass spectrometers have to be pumped which represents a major barrier for extending in situ ion composition measurements downwards into the mesosphere. Such measurements became technically feasible only with the advent of compact high speed cryopumps which could be used on rockets.

The first positive ion composition measurements reaching the mesosphere were made by Narcisi and colleagues [18]. Later on, several research groups contributed to the exploration of the mesospheric plasma, the so called ionospheric D-region. The first negative ion composition measurements in the atmosphere were performed in 1970 independently by Arnold *et al.* [19] and Narcisi *et al.* [20].

Further extension of in situ ion composition measurements into the even denser stratospheric layer required greatly improved mass spectrometric techniques and became feasible only in 1977 using balloon-borne mass spectrometers. The first negative ion composition measurements in the stratosphere were made in 1975 by Arnold and Henschen [21] and positive ions were measured by Arnold *et al.* [22] and Arijs *et al.* [23].

Using balloon-borne mass spectrometers the groups of Arnold and Arijs during the following years explored the region mostly between about 20 and 33 km altitude. Only few measurements extended to heights above 33 km with a maximum height of 45 km [22, 24, 25, 26] and only a few measurements extended to heights below 20 km with a lowermost height around 12 km.

Thus, the balloon work covers the altitude range between about 12 and 45 km but by far most data were obtained only between about 20 and 33 km.

A further extension of ion composition measurements downwards in altitude into the troposphere became feasible only very recently using aircraft-borne mass spectrometers [12, 28, 29, 30]. These measurements which were made by our group at the MPI-K so far cover the altitude range between about 7 and 12 km.

Most recently, in 1984, detailed ion composition measurements could for the first time be performed in the stratopause region by our group [31], using a newly designed parachute-borne dropsonde mass spectrometer payload, which is carried by a rocket up to 60 km altitude and subsequently separated from the rocket motor. Positive and negative ion composition data could be obtained between about 30 and 60 km altitude. Thus, the gap between the regions covered by conventional rocket (above about 60 km) and balloon measurements (below 45-40 km) could be closed.

The purpose of the present paper is to review our current understanding of atmospheric ion chemistry with an emphasis on recent progress in the area of in situ ion composition measurements. Interest will be focussed also on analytical applications and ion-induced aerosol formation.

SOURCES AND SINKS OF STRATOSPHERIC IONS

The only important source of ionization in the stratosphere, under most conditions, is galactic cosmic rays [32]. These are mostly energetic protons having average kinetic energies of about 100-1000 MeV corresponding to an atmospheric penetration depth of about 10-15 km. Thus, the galactic cosmic ray ionization rate, Q, reaches a maximum of about 10-100 cm^{-3} s^{-1} around this altitude.

Since the galactic cosmic rays are partially shielded by the interplanetary and earth's magnetic fields, Q undergoes temporal and spatial variations. It decreases as solar activity increases, and it increases with increasing geomagnetic latitude.

Primary charged species formed by galactic cosmic ray ionization are N^+_2, O^+_2, O^+, N^+, and free electrons. The latter are rapidly attached to gas molecules, giving rise to simple negative ions, mostly O^-_2. Subsequent ion molecule reactions of primary positive and negative ions lead to complex positive and negative cluster ions. Ultimately these are removed by ion-ion recombination involving either a binary or a ternary mechanism [33].

Considerable experimental [33] and theoretical [34] progress has recently been made in determining stratospheric ion-ion recombination coefficients. In particular, it was found that binary ion-ion recombination can be enhanced as the gas pressure increases ("pressure enhanced binary ion-ion recombination") [33].

Taking recent effective ion-ion recombination coefficients α and measured Q-values, the total ion concentration, n, can be calculated from the simple steady-state continuity equation $n = (Q/\alpha)^{1/2}$. Resulting n-values range between about $10^3 - 10^4$ cm^{-3} and are in reasonable agreement with measured n-values recently obtained from improved Gerdien-condenser experiments [35] (Fig. 1).

Ion-recombination lifetimes $t_R = (\alpha n)^{-1}$ range between about $10^2 - 10^4$ s (Fig. 2). When compared with ion lifetimes t_A against collision with aerosols [36] (also shown in Fig. 2), t_R is much smaller throughout the stratosphere.

Consequently, ion attachment to aerosols should not be an efficient loss process for stratospheric ions.

COLLISION PROCESSES OF STRATOSPHERIC IONS

Due to the very large abundance ratio of neutral molecules to ions (about $10^{13} - 10^{14}$ in the middle stratosphere), ion interactions are dominated by ion-molecule collisions. These have cross sections being about 100 times larger than those for molecule-molecule collisions due to relatively long-ranging charge-dipole attraction forces.

Another consequence of these forces is that reactive ion-molecule collisions ("ion-molecule reactions"), in contrast to neutral gas reactions, in many cases do not possess activation energy barriers and thus proceed at the collision rate [37].

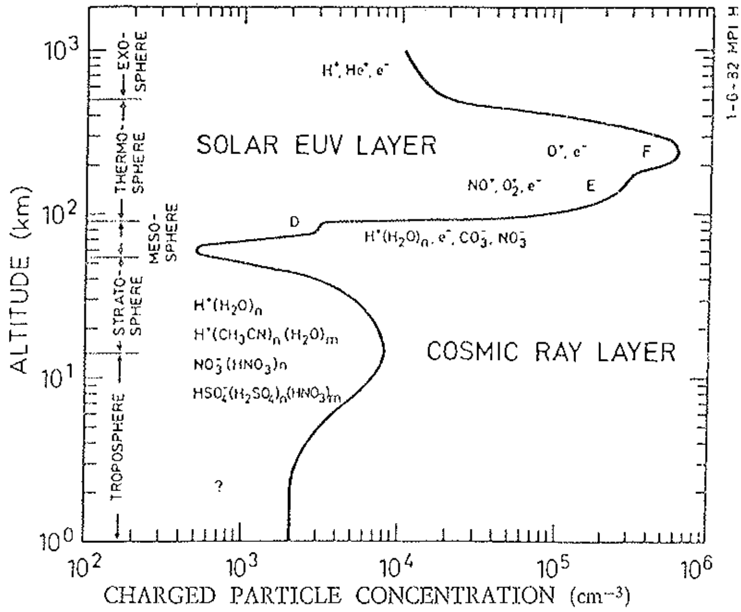

FIG. 1. Schematic representation of atmospheric ionization layers. [After Arnold, Ref. 1].

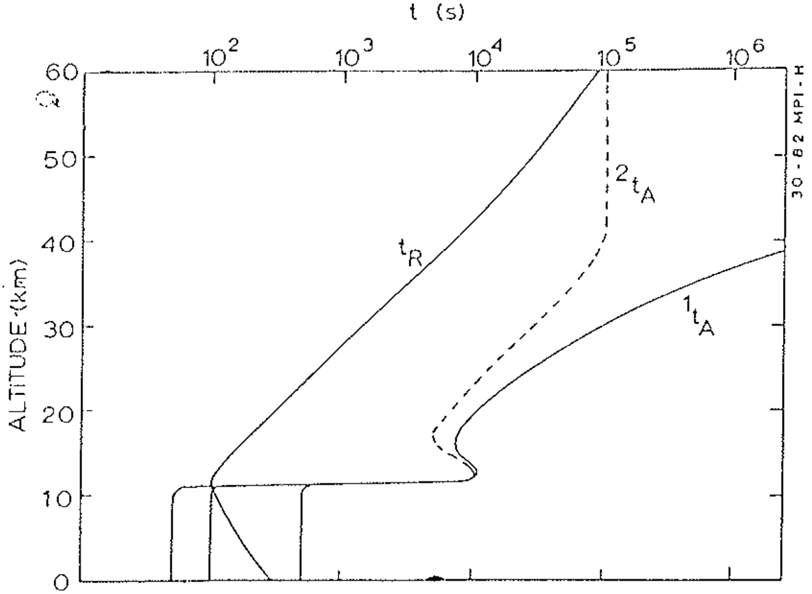

FIG. 2. Typical ion-recombination lifetimes (t_R) compared with free-ion lifetimes against attachment to aerosols (1_{tA}, 2_{tA} "meteor smoke particles" added). [After Arnold, Ref. 1].

Finally, charge-dipole attraction also gives rise to clustering of molecules to ions [38], leading to large cluster ions which ultimately may become condensation nuclei [39]. Interestingly, even cluster ions which contain only a relatively small number of molecules, e.g., 5-10, develop properties similar to those of macroscopic liquid droplets [39].

Under stratospheric conditions, ion clustering proceeds via a ternary mechanism,

$$A^+ + B + M \rightarrow A^+B + M, \tag{1}$$

where M is a collision partner. If there is no kinetic limitation, a thermodynamic equilibrium between processes such as Eq. 1 and thermal dissociation (reverse of Eq. 1) determines the size distribution of $A^+(B)_n$ cluster ions.

A new class of ion-molecule reactions, so-called ion-catalyzed reactions which were only recently [40] studied in the laboratory, may occur in the stratosphere. They involve the reaction of a molecule which is clustered to an ion with a gas-phase atom or molecule. Thus "ion-catalyzed reactions" involving larger cluster ions are somewhat similar to surface catalysis. The reactant molecule may be regarded as being adsorbed on the "surface" of the cluster ion.

When compared with its homogeneous gas-phase analog, an ion-catalyzed reaction may have a rate coefficient which is larger by orders of magnitude. The reactions [40]

$$O_3 + NO \rightarrow NO_2 + O_2 \tag{2}$$

and

$$Na^+O_3 + NO \rightarrow NO_2 + O_2 + Na^+, \tag{3}$$

e.g., have rate coefficients of $1.3 \cdot 10^{-14} - 2.1 \cdot 10^{-17}$ cm^3 s^{-1} (depending on temperature) and $6.5 \cdot 10^{-11}$ cm^3 s^{-1}, respectively.

Besides interacting with molecules, stratospheric ions preferably interact with oppositely-charged ions due to very long-ranging Coulomb-attraction forces.

Besides giving rise to free ion removal, ion-ion recombination may also lead to the formation of stable ion pairs [42] which by ion attachment may grow to polyions [43]. The polyions are still hypothetical as they have neither been detected in the laboratory nor in the atmosphere. If existent, they may play a role as precondensation nuclei [42].

Thus, ions may promote aerosol formation in two ways, by conventional ion nucleation involving ion clustering and by polyion nucleation.

ION CHEMISTRY

Positive Ions

The most abundant stratospheric positive ions are $H^+(H_2O)_n$ and $H^+(CH_3CN)_\ell(H_2O)_m$ cluster ions with the former dominating above about 35 km and the latter becoming most prominent below this altitude (Fig. 3).

Besides these major ions, various minor ion species were detected

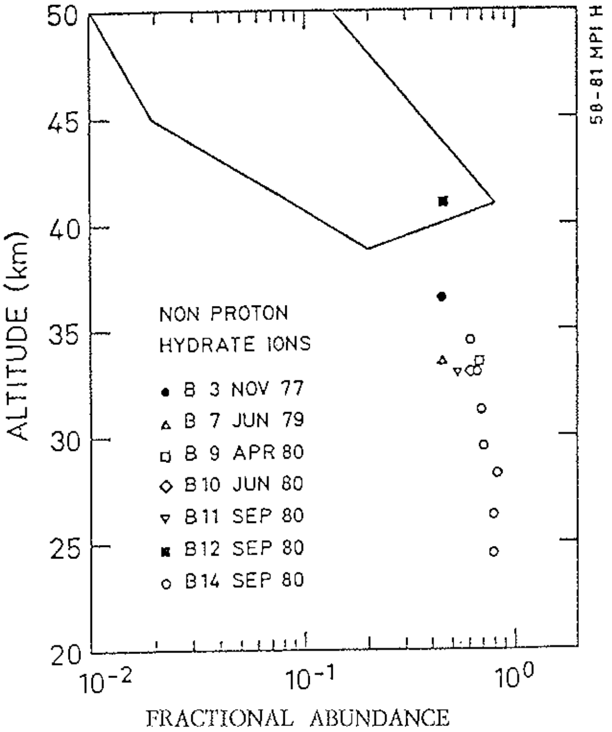

FIG. 3 - Fractional abundance of positive ions not belonging to the $H^+(H_2O)_n$ family [after Henschen and Arnold; Ref. 43, and Schlager and Arnold, unpublished material].

(Table 1), possibly also containing molecules such as CH_3OH. In addition, very massive positive ions (upt to about 320 atomic mass units) were detected but could as yet not be identified.

The chemical evolution of stratospheric positive ions may be viewed as proceeding in three stages. The first stage involves reactions of primary positive ions (N^+, O^+_2, O^+, N^+) with major gases (N_2, O_2) leading to O^+_4 and NO^+ (Fig. 4). The fractional rates of formation for these ions are about 90% and 10%. The time scale for stage one is only on the order of 10^{-5} s in the middle stratosphere (if not otherwise indicated, time scales given hereafter refer to an altitude of 35 km).

Stage two involves reactions of major trace gases, mostly H_2O leading to $H^+(H_2O)_n$ cluster ions. It is essentially the large proton affinity of the water molecule and the strong bonding of H_2O-molecules to the hydro-

TABLE 1 - *Stratospheric positive ion species detected by balloon-borne mass spectrometers* (Schlager and Arnold, submitted for publication).

Ion	Mass	Ion	Mass
H_3O^+	19	$H^+CH_3CN\,(H_2O)_2$	104 ± 1
Na^+	23 ± 1	$H^+\,(H_2O)_6$	109
H^+HCN	29 ± 2	$H^+CH_3OH\,(H_2O)_2$	110 ± 1
$H^+\,(H_2O)_2$	37	$H^+CH_3CN\,(H_2O)_4$	114 ± 1
H^+CH_3CN	42		117 ± 1
$H^+HCN \cdot H_2O$	45 ± 1	$H^+\,(CH_3CN)_2\,(H_2O)_2$	119
$H^+CH_3OH \cdot H_2O$	49 ± 1		121 ± 1
$H^+\,(H_2O)_3$	55		125 ± 1
$Na^+\,(H_2O)_2$	58 ± 1		128 ± 1
$H^+CH_3CN \cdot H_2O$	60		134 ± 2
$H^+HCN\,(H_2O)_2$	63 ± 1		139 ± 2
$H^+CH_3OH\,(H_2O)_2$	67 ± 1	$H^+H_2O\,(CH_3CN)_3$	142 ± 1
$H^+\,(H_2O)_4$	73		151 ± 2
$H^+CH_3CN\,(H_2O)_2$	78		158 ± 3
$H^+HCN\,(H_2O)_3$	81 ± 1		168 ± 3
$H^+\,(CH_3CN)_2$	83		179 ± 3
$H^+CH_3OH\,(H_2O)_3$	86 ± 1		182 ± 3
$H^+\,(H_2O)_5$	91		186 ± 3
$H^+CH_3CN\,(H_2O)_3$	96		190 ± 3
$H^+\,(CH_3CN)_2\,H_2O$	101		202 ± 3

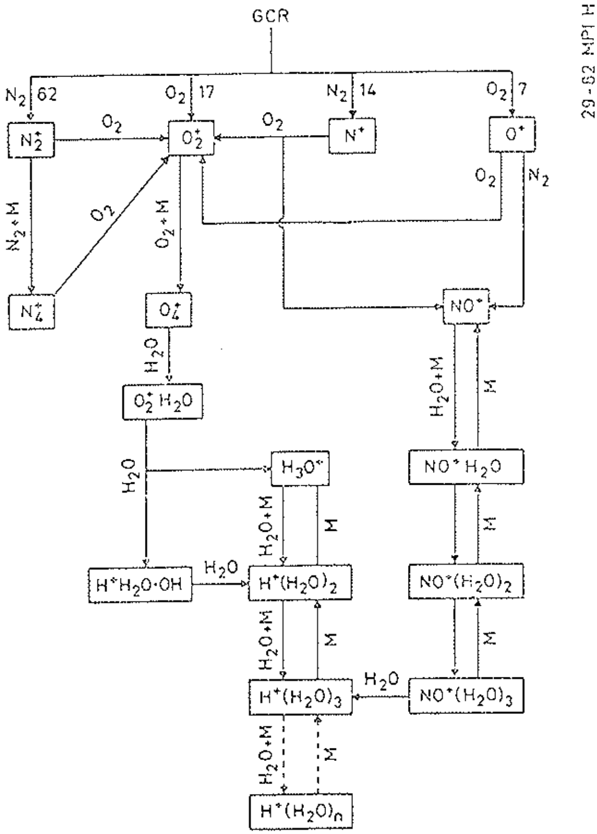

FIG. 4. Stratospheric positive ion reaction scheme (stages one and two) [after Ref.'s 13, 14].

nium ion, H_3O^+, which drive the formation of $H^+(H_2O)_n$ ions. Due to the relatively large abundance of water vapor a quasi-equilibrium size distribution of $H^+(H_2O)_n$ is rapidly established. Usually, the distribution peaks around $n = 4$ or 5 in the middle stratosphere, depending somewhat on temperature. The time scale for stage two is only on the order of 10^{-3} s, which is much smaller than the ion-recombination lifetime, t_R (see Fig. 2).

Stage three (Fig. 5) involves reactions of very low abundance trace gases having time scales which are on the order of t_R or even larger. Consequently, the abundance ratio for product ions and precursor ions never becomes very much larger than one.

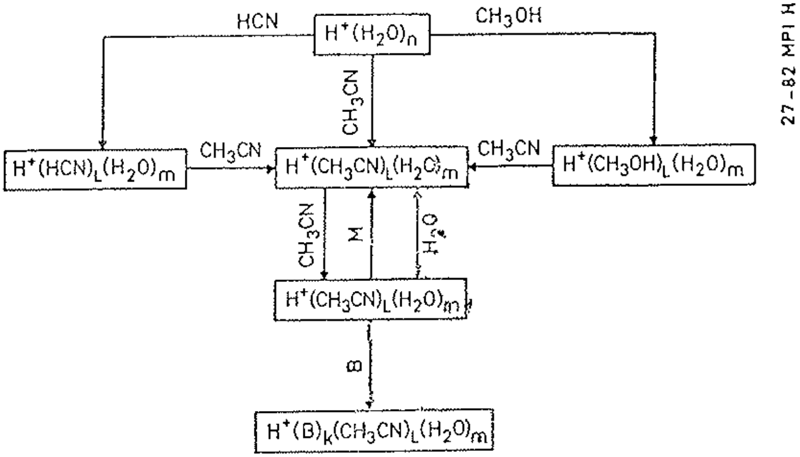

FIG. 5. Stratospheric positive ion reaction scheme (stage three).

These trace gases all have proton affinities substantially larger than that of H_2O (170 kcal mole^{-1}) and thus can react with $H^+(H_2O)_n$ ions via

$$H^+(H_2O)_n + C \rightarrow H^+C(H_2O)_{n-1} + H_2O. \qquad (4)$$

Equation 4 is not a simple proton-transfer reaction but rather involves displacement of an H_2O molecule contained in an $H^+(H_2O)_n$ cluster ion by a molecule C. Usually, C must have a substantially larger proton affinity than H_2O (170 kcal mole^{-1}) in order to make Eq. 4 exothermic [13, 14]. This is true because H_2O-molecules mostly bond more strongly to H_3O^+ than to H^+C.

Among the reactant molecules, C acetonitrile, CH_3CN, which has a proton affinity PA $(CH_3CN) = 186$ kcal mole^{-1} seems to be the most important [22, 41]. Reactions such as Eq. 4 involving CH_3CN lead to $H^+CH_3CN(H_2O)_m$ mixed cluster ions. Subsequent displacement of H_2O-ligands by CH_3CN via

$$H^+(CH_3CN)_\ell(H_2O)_m + CH_3CN \rightarrow H^+(CH_3CN)_{\ell+1}(H_2O)_{m-1} + H_2O \qquad (5)$$

may occur. According to in situ observations and laboratory studies [33, 41, 47], however, it seems that the exothermicity of Eq. 5 decreases as ℓ increases.

Under stratospheric conditions ℓ is usually not larger than two to three. The total number of molecules attached to H^+CH_3CN is about the the same as the number of H_2O-ligands attached to H_3O^+-cores.

It was also found from laboratory studies [41], that $H^+(CH_3CN)_3H_2O$ is a particularly stable cluster. This is probably due to a symmetric structure witb an H_3O^+-core having a delocalized positive charge shared by its three hydrogen atoms to each of which a CH_3CN molecule is attached.

Mixed cluster ions of the type $H^+CH_3CN\,(H_2O)_n$ react also with other large proton affinity molecules such as CH_3OH via

$$H^+CH_3CN\,(H_2O)_n + CH_3OH \rightarrow H^+CH_3CN \cdot CH_3OH\,(H_2O)_{n-1} + H_2O, \quad (6)$$

leading to even more complex heteromolecular cluster ions.

Generally, the competitive gas-phase solvation of the proton seems to favor H_2O in the outer "shell" of the cluster. This is probably due to the strong hydrogen bonding of H_2O, which is also responsible for the large heat of vaporization of bulk water.

If present in the stratosphere, NH_3, due to its very large proton affinity, should efficiently react with $H^+\,(CH_3CN)_\ell\,(H_2O)_m$ ions. Recent laboratory studies [44] indicate large rate coefficients for these processes.

Other molecules with a high proton affinity which have been discussed [44, 13, 45] as potential reactants for stratospheric positive cluster ions are metal compounds such as NaOH or NaCl. It is thought that these are formed in the mesosphere from meteor ablation material which is mixed downwards into the stratosphere.

According to laboratory studies [46], NaOH and NaCl both react with $H^+\,(H_2O)_n$ ions, leading to $Na^+\,(H_2O)_n$ cluster ions.

From the failure to detect the latter ion species in the middle stratosphere, it was concluded [47, 48] that NaOH and NaCl are not present in gaseous form but probably are converted to some kind of aerosols before they reach the middle stratosphere.

An alternative possibility is that strongly polar compounds such as NaCl form dimers or higher polymers which by reaction with $H^+\,(H_2O)_n$ ions do not lead to simple $Na^+\,(H_2O)_n$ cluster ions but to more complex clusters containing two or more metal atoms.

Acetonitrile, the most important reactant molecule involved in stage three of the positive ion evolution, seems to originate from the troposphere (see section on Analytical and Diagnostic Applications of In Situ Ion Composition Measurements) as discussed by Henschen and Arnold [43].

Recently, this view received strong support from laboratory studies suggesting that CH_3CN hardly reacts with OH [43, 49] and is not photodissociated hy UV-radiation reaching the middle stratosphere [50]. Thus, if formed in the troposphere, CH_3CN should he capable of reaching the middle stratosphere. However, the possibility exists that CH_3CN, due to its relatively large solubility in water, may efficiently be rained or washed out in the troposphere [49].

The tropospheric source of CH_3CN as yet has not been identified with certainty. Biomass burning has been discussed [50] as a potential CH_3CN source.

Kinetic and thermodynamic data on ion reactions involved in stages one and two are to a large extent available [51]. By contrast, only few data are available for stage three processes.

In summary, it seems that our understanding of the stratospheric positive ion chemistry is far from satisfactory because independent information on both underlying processes and reactant trace gases is largely lacking.

Negative Ions

The most abundant negative ion species observed in the stratosphere can be grouped [21] in two main families, $NO^-_3(HNO_3)_n$ and $HSO^-_4(H_2SO_4)_\ell(HNO_3)_m$, with the latter being dominant above about 25-30 km (Fig. 6). Besides these major ions various minor negative ion species [52, 53] were detected (Table 2). These are mostly cluster ions containing high electron affinity core molecules such as CN and CO_3 and high gas phase acidity ligand molecules such as HCl, HNO_2, HOCl, and HSO_3. Water molecules are also present as ligands.

Usually, the $NO^-_3(HNO_3)_n$ ions contain about two to three HNO_3-ligands. Major $HSO^-_4(H_2SO_4)_\ell(HNO_3)_m$ ions may contain up to three H_2SO_4 ligands.

Recently [53] it was found that larger $HSO^-_4(H_2SO_4)_n$ ions are markedly hydrated, suggesting an increase of the H_2-bond energy for increasing n.

The chemical evolution of stratospheric negative ions, like that of positive ions, may be viewed as proceeding in three stages.

Stage one (Fig. 7) involves reactions of the major gas, O_2, leading to O^-_4 (time scale: 10^{-3} s). Stage two (Fig. 7) involves reactions of relatively abundant trace gases such as CO_2, O_3, and H_2O, leading mostly to CO^-_3 ions and its hydrates (time scale $\leq 10^{-3}$ s). Since the latter time scale is

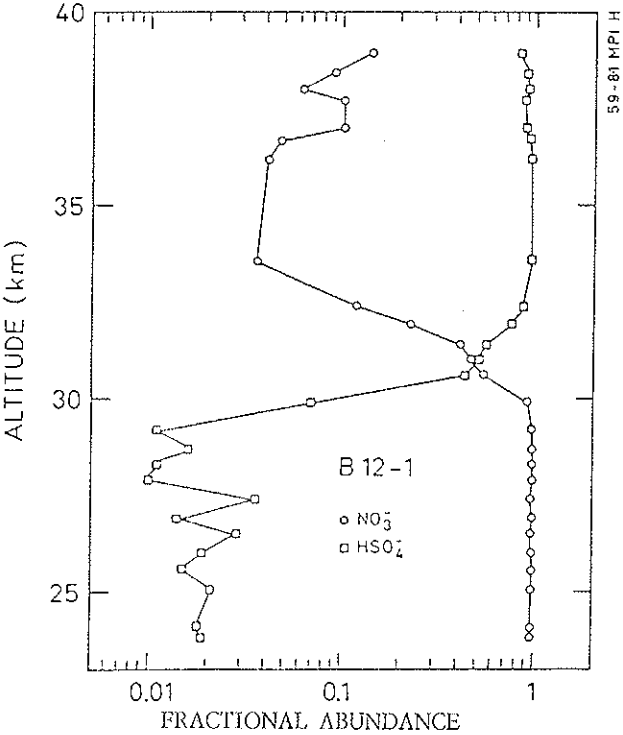

FIG. 6. Fractional abundance of major negative cluster ion families containing NO^-_3 and HSO^-_4 cores [54].

TABLE 2 - *Stratospheric negative ion species detected by balloon-borne mass spetrometers* [52, 53].

Mass	Ion	Mass	Ion
26±2	CN^-	223±1	$HSO^-_4 (HNO_3)_2$
43±2	$CN^- H_2O$	241±1	$HSO^-_4 (HNO_3)_2 H_2O$
61±1	CO^-_3, NO^-_3	251±1	$NO^-_3 (HNO_3)_3$
80±2	$CO^-_3 H_2O, NO^-_3 H_2O$	258±1	$HSO^-_4 \cdot H_2SO_4 \cdot HNO_3$
97±1	HSO^-_4	274±1	$HSO^-_4 (HNO_3)_2 HClO$
109±2	$NO^-_3 HNO_2$		$HSO^-_4 \cdot H_2SO_4 \cdot HSO_3$
125	$NO^-_3 HNO_3$	286±1	$HSO^-_4 (HNO_3)_3$
133±1	$HSO^-_4 (H_2O)_2$	293±1	$HSO^-_4 (H_2SO_4)_2$
	$HSO^-_4 HCl$	374±1	$HSO^-_4 (H_2SO_4)_2 HSO_3$
143±1	$NO^-_3 HNO_3 H_2O$	391±1	$HSO^-_4 (H_2SO_4)_3$
148±2	$HSO^-_4 HOCl$	409±1	$HSO^-_4 (H_2SO_4)_3 H_2O$
160	$HSO^-_4 HNO_3$	427±1	$HSO^-_4 (H_2SO_4)_3 (H_2O)_2$
174±1	$NO^-_3 HNO_3 HNO_2$	454±1	$HSO^-_4 (H_2SO_4)_3 HNO_3$
188	$NO^-_3 (HNO_3)_2$	472±1	$HSO^-_4 (H_2SO_4)_3 HSO_3$
195	$HSO^-_4 H_2SO_4$	489±1	$HSO^-_4 (H_2SO_4)_3 HSO_3 H_2O$
206±1	$NO^-_3 (HNO_3)_2 H_2O$		

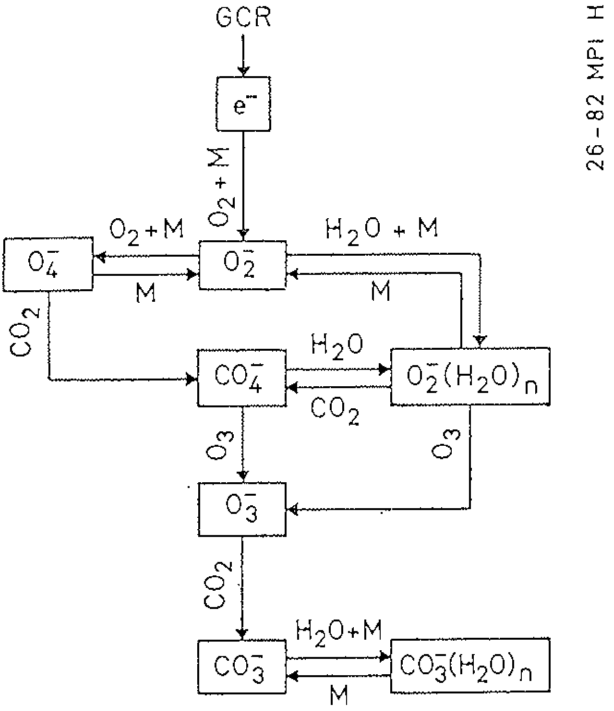

FIG. 7. Stratospheric negative ion reaction scheme (stages one and two) [after Ref. 13].

usually much smaller than the ion recombination lifetime, t_R, CO_3^- and its hydrates are further converted by reactions with less abundant trace gases, mostly NO_x (NO, NO_2, HNO_3, N_2O_5). This leads to the formation of $NO_3^-(HNO_3)_n$ cluster ions (stage three, Fig. 8).

Since the HNO_3-vapor concentration is sufficiently large in the stratosphere, a quasi-equilibrium size distribution of $NO_3^-(HNO_3)_n$ is established, peaking around $n = 2$ or 3.

The second part of stage three involves reactions with sulfur-bearing gases, mostly H_2SO_4 and HSO_3, leading to HSO_4^--cores. Subsequently, H_2SO_4 displaces HNO_3-ligands, leading to $HSO_4^-(H_2SO_4)_\ell(HNO_3)_m$ mixed cluster ions. As ℓ becomes larger than about two, these cluster ions are markedly hydrated. This probably reflects strong cooperative bonding effects between H_2SO_4- and H_2O-ligands. In this respect, the cluster ion

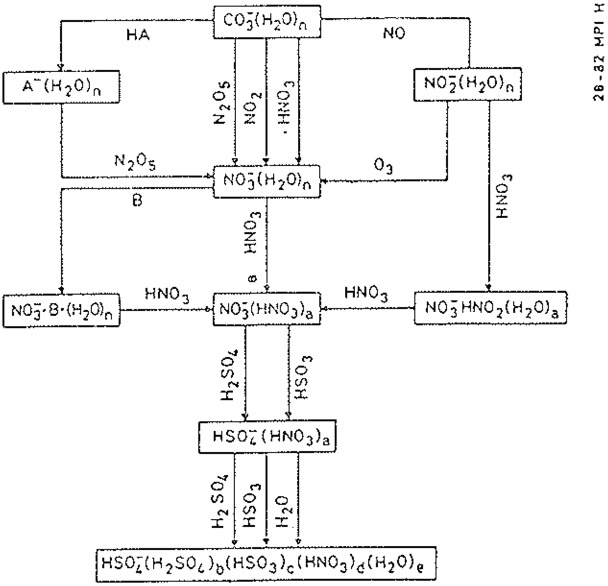

FIG. 8. Stratospheric negative ion reaction scheme (stage three).

already resembles a small solution droplet composed of an H_2SO_4/H_2O mixture which has a large heat of mixing.

The NO_x-reactant gases leading to $NO^-_3(HNO_3)_n$ ions are formed in the stratosphere by photochemical processes mostly from the precursor gas N_2O which is of tropospheric origin. The sulfur-bearing reactant molecules H_2SO_4 and HSO_3 are also formed in the stratosphere by photochemical and/or heterogeneous processes. Here, the most important precursor gas seems to be OCS which is also of tropospheric origin [55]. During volcanically very active periods SO_2 may also become an important precursor gas.

Kinetic and thermodynamic data for negative ion reactions involved in stages one and two are to a large extent available from laboratory studies [51]. Stage three data are mostly lacking.

Thus, our understanding of stratospheric ion chemistry, like that of positive ion chemistry, is far from satisfactory due to the lack of independent information on reactant trace gases and laboratory data.

POTENTIAL ROLE OF IONS IN STRATOSPHERIC TRACE GAS AND AEROSOL PROCESSES

Trace gases can be formed, destroyed, or removed from the gas phase by ion processes including ion-molecule reactions, ion-ion recombination, and ion nucleation.

Trace gas destruction is limited by the relatively small total ion concentration, n. Taking an upper limit of $k = 10^{-9}$ cm^3 s^{-1} as the rate coefficient for an ion-molecule collision, a lower limit of about one day is obtained for the lifetime of a molecule against destruction or removal by ion processes. For noncatalytic ion processes the lifetime can be much larger.

Trace gas formation by noncatalytic ion processes is limited by the total ionization rate, Q, being on the order of 10-100 cm^{-3} s^{-1}. For catalytic processes the upper limit to the rate of trace gas molecule formation is $k\ n$ [B], or about 10^{-5} [B], where [B] is the concentration of the reactant molecule.

Ions may also promote aerosol formation via ion nucleation. Basically two processes, conventional ion nucleation, IN [39, 42], and polyion nucleation, PIN [42] have been discussed (see also section on COLLISION PROCESSES OF STRATOSPHERIC IONS). IN, although suffering from severe kinetic limitations, may represent a potential source for stratospheric condensation nuclei [39]. IN rates may become particularly large around 30-35 km altitude during sudden winter coolings following major stratospheric warmings. Under these conditions, due to large [H_2SO_4] values, kinetic limitations of IN may be markedly reduced.

Thus, a seed layer of condensation nuclei may be formed around 30-35 km altitude. Even under conditions of a condensation-evaporation equilibrium, IN may be sufficiently efficient to maintain the stratospheric aerosol layer [39] (Fig. 9).

If ions were, in fact, involved in stratospheric aerosol formation, a physical link between solar activity and the stratospheric aerosol layer may exist [39].

ANALYTICAL AND DIAGNOSTIC APPLICATIONS OF IN SITU ION COMPOSITION MEASUREMENTS

Atmospheric ions react selectively with certain neutral trace gases leading to characteristic product ion species. By measuring reactant and

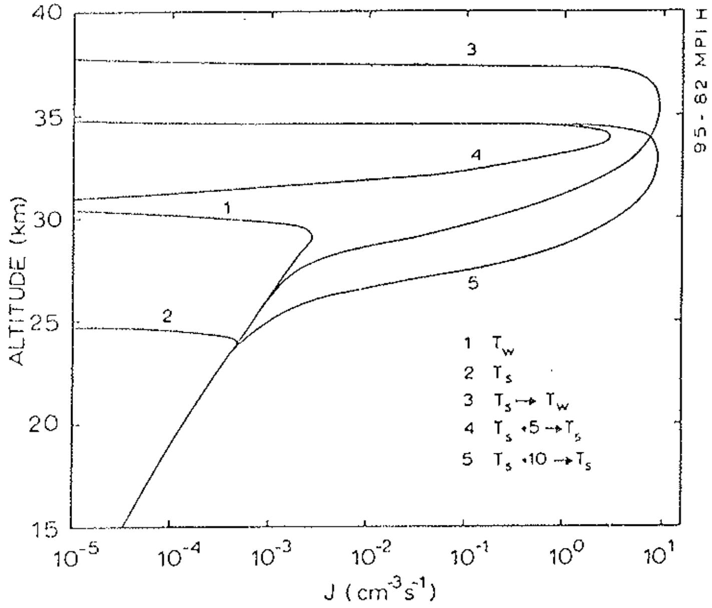

FIG. 9. Ion-nucleation rates as calculated by Arnold (see [39]) for winter [1], summer [2], and stratospheric winter warming-cooling events [3, 4, 5].

product ions in situ, the number densities of the reactant trace gases can be inferred with great sensitivity. This indirect method for atmospheric trace gas detection was termed PACIMS (passive chemical ionization mass spectrometry) [56].

The extremely large sensitivity of PACIMS is due to both the relatively large ion-recombination lifetime, t_R, and the large rate coefficients, k, for ion-molecule reactions. Assuming that an ion, C^+, is formed by

$$A^+ + B \rightarrow C^+ + D \tag{7}$$

and lost preferably by ion-ion recombination, a steady-state treatment yields

$$[B] = [C^+] / [A^+] (k\, t_R).$$

Taking $k = 10^{-9}$ cm^3 s^{-1}, $t_R = 10^4$ s, and a minimum measurable ion abundance ratio, $[C^+] / [A^+] = 10^{-4}$, one obtains a minimum detectable

[B] = 10 cm^{-3} corresponding to a volume mixing ratio on the order of 10^{-16} in the middle stratosphere.

Various trace gases (Table 3) have already heen detected using PACIMS. Particularly interesting ones are H_2SO_4 and HSO_3, as they are involved in stratospheric aerosol formation (Fig. 10).

It seems that H_2SO_4-vapor is supersaturated with respect to H_2SO_4-H_2O solution droplets at altitudes below about 30-35 km depending on season. Thus, H_2SO_4-H_2O aerosols can exist only below these heights. It also seems that HSO_3 becomes abundant at the lower heights, possibly suggesting [53, 56] that aerosols are formed from HSO_3^- rather than H_2SO_4-vapor. It is conceivable that H_2SO_4 is formed in the aerosols rather than in the gas phase, which would be in contrast to most current models of the stratospheric sulfur chemistry.

This example clearly demonstrates the kind of interesting new information on trace gases which was recently obtained from stratospheric in situ ion composition measurements.

Very recently, active chemical ionization mass spectrometry (ACIMS) was employed for stratospheric trace gas detection [57]. Here ions are created in the stratospheric medium by an electron bombardment ion

TABLE 3 - *Stratospheric trace gases detected by chemical ionization mass spectrometry. Altitude range and positive (PI) or negative (NI) ion composition measurements are indicated. Parentheses (+) denote that identification is uncertain.*

Trace gas	PI	NI	Altitude Range
H_2O	+	+	33 - 42
CH_3CN	+		15 - 42
CH_3OH	+		15 - 34
CH_3NO_2	(+)		15 - 34
HNO_3		+	33 - 42
HCN		(+)	34
HSO_3		+	28 - 34
H_2SO_4		+	15 - 40
HNO_2		(+)	34

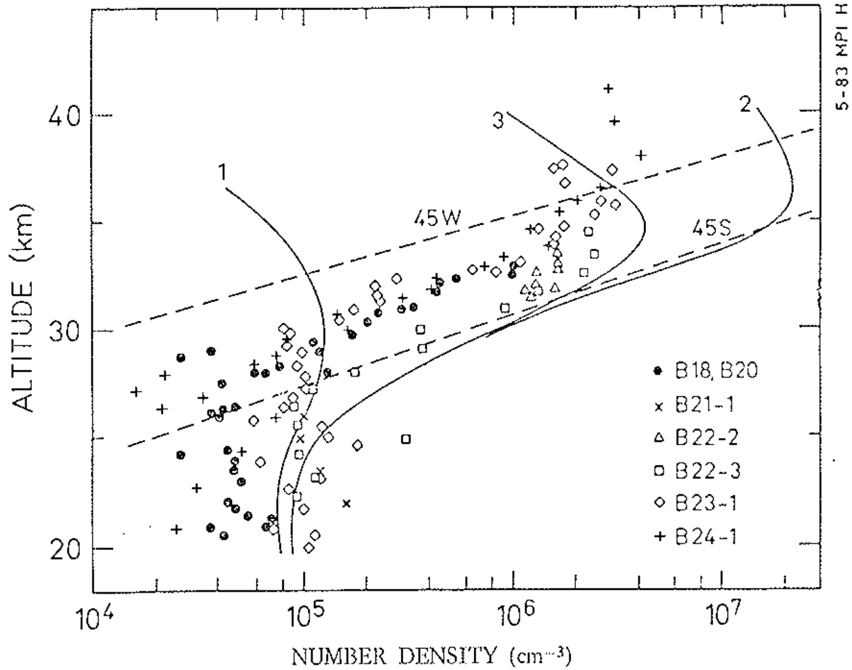

FIG. 10. Sulfuric acid vapor abundances as obtained by passive chemical ionization mass spectrometry. Curves 1, 2, and 3 are model predictions of Turco *et al.* [58]. Broken curves are equilibrium saturation vapor concentrations for 45° latitude summer (S) and winter (W). (Figure from Qiu and Arnold, Ref. [26]).

source and sampled by an ion mass spectrometer after they have flown with the neutral gas over a distance of about 50 cm. The ions reside for about 20 seconds in the medium before they are sampled. Within this time, they react with trace gases whose concentration can be inferred from the measured abundances of reactant and product ions.

ACIMS has already provided information on HNO_3, H_2SO_4, CH_3CN, and H_2O [57]. Since the large cluster ions interact with condensable vapors similar to aerosols, in situ compositional measurements of large compositional cluster ions also provide interesting information on the composition and thermodynamics of aerosols which exist in the same medium [53]. It was found that large negative cluster ions around 30 km altitude are composed mostly of H_2SO_4 and H_2O which is rather similar to the expected aerosol composition. Bond energies for H_2SO_4-ligands were found to be about 20 kcal mole^{-1} which is close to the heat of vaporization for a bulk H_2SO_4-H_2O solution. It was also found that the HSO_3-radical bonds similarly strongly to large negative ion clusters such as H_2SO_4. This finding is of great interest as no laboratory information on HSO_3 is as yet available.

Thus, in situ ion composition measurements can provide new and interesting information on neutral trace gases and aerosols.

ASSESSMENT OF TROPOSPHERIC ION CHEMISTRY

The nature of tropospheric ions and their possible role in trace gas and aerosol processes is, as already mentioned, largely unknown. Building on recent progress in our understanding of stratospheric ion processes and first in situ ion composition measurements which were recently made in the upper troposphere, an assessment of tropospheric ion chemistry will be attempted in the following section.

In the troposphere the most important sources of ionization are radioactivity and galactic cosmic rays [60]. The former, which is due to α, β, and γ radiations from thoron and radon, is dominant up to about one kilometer altitude. Above this height, as in the stratosphere, galactic cosmic ray ionization is most important.

The total ionization rate, Q, is on the order of 1-10 $cm^{-3}\ s^{-1}$ in the troposphere.

Removal of free ions occurs by two mechanisms: ion-ion recombination (essentially saturated ternary ion-ion recombination; effective binary coefficient $\alpha = 2 \cdot 10^{-6}\ cm^3\ s^{-1}$) and ion-attachment to aerosol particles. The latter process leads to so-called "large ions" which are, in fact, electrically-charged aerosols rather than ions in a strictly physical sense [60]. Usually, ion-attachment is the most important sink for free ions throughout the troposphere as the tropospheric aerosol content is relatively large (Fig. 2). In this respect, the tropospheric ionization-deionization balance differs greatly from the stratospheric one.

On the average, the free ion lifetime in the troposphere is on the order of 10^2-10^3 seconds. Taking typical Q-values of 1-10 $cm^{-3}\ a^{-1}$, a steady-state free ion concentration, n, on the order of 10^2-$10^4\ cm^{-3}$ is obtained. Due to temporal and spatial changes of the aerosol content, tropospheric free ion concentrations may undergo marked changes.

The chemical evolution of tropospheric free ions is rather uncertain. Stages one and two of the positive and negative ion evolutions may be similar to those occurring in the stratosphere. A marked difference, however, may arise from the relatively large tropospheric water vapor abundance possibly leading to marked hydration as early as stages one and two. It is conceivable that in certain cases hydration changes the reactivity of the core ion. For example, reaction of $O^-_3(H_2O)_n$ with CO_2 is much slower or even inefficient compared to that of O_3 [37].

For typical ground level conditions the most prominent positive and negative ions should contain about 10-20 water molecules. This has been found from mass spectrometric studies of ions created in ground level air carried out by our group (unpublished data).

Most uncertain, however, are stages three of the positive and negative ion evolutions, particularly as reactant trace gases are not known. Taking the above free ion lifetimes of 10^2-10^3 seconds and a maximum rate coefficient for an ion molecule reaction on the order of 10^{-9} cm^3 s^{-1}, reactant trace gases having abundances of only 10^6-10^7 cm^{-3} (corresponding volume mixing ratio: 10^{-16}-10^{-15}) can convert a significant fraction of the free ion population.

Potential reactant trace gases may, as in the stratosphere, include molecules possessing large proton affinities or large gas phase acidities. A major difference, however, arises from the fact that trace gases which can be depleted by heterogeneous interaction with aerosols may have small and possibly strongly variable abundances. Such interactions may involve condensation, dissolution, or surface as well as liquid phase chemical reactions.

Since such trace gases seem to be particularly efficient reactants for ions, it is conceivable that the tropospheric ion composition responds sensitively to aerosol conditions and meteorological factors.

This may be illustrated by discussing a possible influence of sulfuric acid vapor, which is a potential reactant trace gas. It may react with negative ions leading to $HSO^-_4(H_2SO_4)_\ell(H_2O)_m$ mixed clusters, and it may also react with large positive water clusters leading to a ligand "shell" composed of a mixture of H_2SO_4 and H_2O.

In the troposphere, sulfuric acid is formed from sulfur-bearing precursor gases and ultimately leads to H_2SO_4-H_2O aerosol solution droplets, as in the stratosphere. However, in contrast to the tropospheric situation, significant H_2SO_4 supersaturation with respect to the H_2SO_4-H_2O phase should occur not under all conditions. Thus, the atmospheric H_2SO_4-vapour concentration should be roughly equal to the equilibrium saturation concentration over the aerosol which depends critically on the relative humidity and on temperature. Consequently, the influence of tropospheric sulfuric acid vapour on the ground level ion composition may vary from negligible to important, depending on conditions.

This example demonstrates the possible response of tropospheric ions to aerosol and meteorological conditions.

Other potential reactant trace gases besides H_2O and H_2SO_4 are NH_3, CH_3CN, and acids such as HNO_3 and HCl. Ammonia, for example, is highly soluble in water and therefore may become depleted from the gas phase. According to in situ measurements, tropospheric ammonia vapor abundances greatly exceed the critical reactant trace gas level. Consequently, NH_3 may markedly influence the positive ion chemistry. The same may be true for CH_3CN which seems to originate from the troposphere.

Thus, positive mixed cluster ions of the type $NH^+_4\,(NH_3)_k\,(CH_3CN)_\ell\,(H_2O)_m$ may be formed. However, it is conceivable that other trace gases which have the potential to react with positive cluster ions are also present in sufficiently large abundances.

For both NH_3 and CH_3CN it was found in the laboratory [44, 59] that only a few molecules can be incorporated into the cluster, forming an "inner" ligand shell, and that H_2O becomes the preferred ligand in the "outer" ligand shell.

Potential reactant gases for negative ions under conditions of low H_2SO_4-vapor abundances are acids such as HNO_3, HCl, and HNO_2, where mixed cluster ions of the type $NO^-_3\,(HNO_3)_\ell\,(H_2O)_m$ may be most prominent.

In order to investigate tropospheric ion chemistry, several so-called "simulation experiments" involving ionization of laboratory air at atmospheric or elevated pressures and subsequent ion detection by differentially-pumped mass spectrometers have been carried out during recent years. However, due to the comparatively small ion residence times encountered in these experiments as a result of ion losses to the walls of the apparatus, at best only stages one and two of the ion evolution can be simulated. The decisive stage three which determines the nature of the terminal ions cannot be simulated as its characteristic time scale of 10^2-10^3 s is much larger than the ion residence time. Therefore, these "simulation studies" have to be interpreted with care.

The first in situ ion composition measurements in the upper troposphere which were recently made by our group [12, 28] using an aircraft-borne mass spectrometer revealed the presence of large negative and positive cluster ions.

Observed negative ion masses and tentative ion identifications are given in Table 4. It appears that the major species can be grouped in two families containing NO^{-}_{3} and HSO^{-}_{4} cores with NHO_3 and other acidic ligands.

Measured fractional count rates are shown in Figure 11. At the upper heights, NO^{-}_{3}-clusters are most prominent while HSO^{-}_{4}-clusters become about equally abundant at the lower altitudes.

Observed positive ion masses are given in Table 5 along with tentative ion identifications. These ions are mostly fragments of larger ambient cluster ions. Electric field dissociation was intendedly employed in order to facilitate ion identification. Other measurements [28] not using the dissociation revealed the presence of much larger positive ions which, however, were difficult to identify due to a lower mass resolution setting.

It appears that the major positive ions around the tropopause are $H^{+}(H_2O)_n$ clusters and cluster species which may fit the $H^{+}(CH_3CN)_{\ell}(H_2O)_m$ sequence. So far, no definitive indication for NH^{+}_{4} cores exists in this region.

As in the stratosphere, the ions can be used as probes for neutral

TABLE 4 - *Negative ion masses as measured in the upper troposphere. Maximum fractional count rates and tentative ion identifications are also given* (after Heitmann and Arnold; Ref. 12).

Mass	Max.	Ion
62 ± 3	22.2	NO^{-}_{3}
80 ± 3	3.8	$NO^{-}_{3}H_2O$
125 ± 2	22.2	$NO^{-}_{3}HNO_3$
143 ± 3	2.4	$NO^{-}_{3}HNO_3 \cdot H_2O$, $(NO_3HSO_3)^{-}$
160 ± 3	15.0	$HSO^{-}_{4}HNO_3$
188 ± 2	66.7	$NO^{-}_{3}(HNO_3)_2$
209 ± 3	22.6	$HSO^{-}_{4}(HNO_3)_2H_2O$; $HSO^{-}_{4}HSO_3H_2O$; $HSO^{-}_{4}HSO_5$
223 ± 2	11.3	$HSO^{-}_{4}(HNO_3)_2$
241 ± 3	14.3	$HSO^{-}_{4}(HNO_3)_2H_2O$; $HSO^{-}_{4}HSO_3 \cdot HNO_3$
251 ± 3	5.7	$NO^{-}_{3}(HNO_3)_3$
273 ± 3	7.5	$HSO^{-}_{4}(HNO_3)_3H_2O$; $HSO^{-}_{4}HSO_3HNO_3H_2O$; $HSO^{-}_{4}HSO_5 \cdot HNO_3$
286 ± 3	2.6	$HSO^{-}_{4}(HNO_3)_3$
297 ± 3	2.7	$HSO^{-}_{4}(H_2SO_4)_2$
352 ± 3	2.1	$HSO^{-}_{4}(H_2SO_4)_2HNO_3$

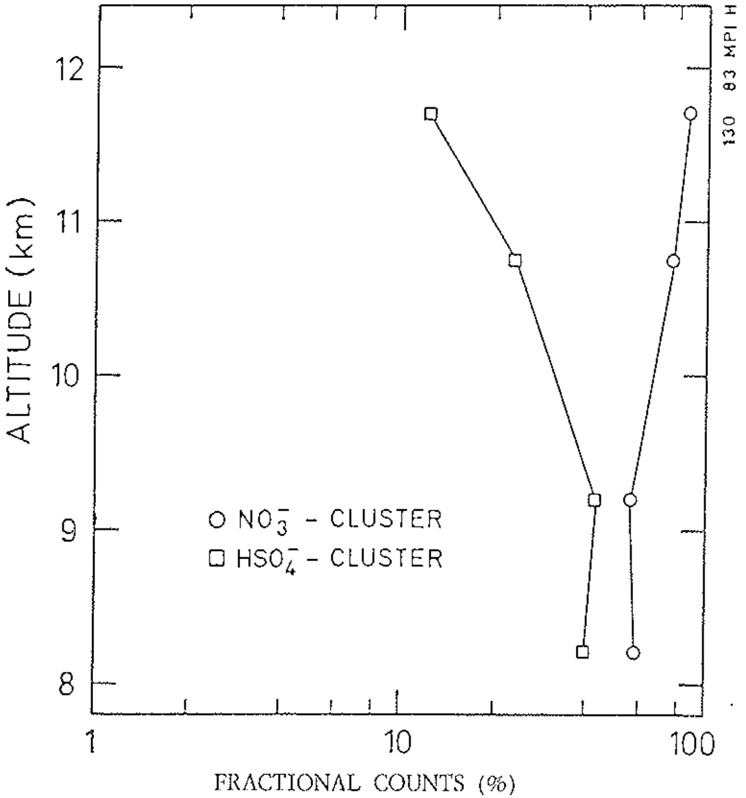

FIG. 11. Total fractional count rates for NO^-_3 and HSO^-_4 cluster ions as measured in flights F1 and F2 [after Heitmann and Arnold; Ref. 12].

trace gases. Attempts to infer HNO_3 and H_2SO_4 are shown in Figures 12 and 13. The HNO_3-data fill an observational gap which existed between about 7 km and the stratopause. They fall mostly into the range of model predictions. However, more measurements are needed also due to the expected variability of HNO_3-abundances induced by heterogeneous removal of this trace gap.

The sulfuric acid vapour measurements (Figure 13) are the first ones in the troposphere. They compare also reasonably well with model predictions. In particular, they reveal that H_2SO_4-vapour appears to be highly supersaturated with respect to the condensed H_2SO_4/H_2O phase which is important for nucleation considerations. For a more detailed discussion of HNO_3-and H_2SO_4-data see reference [12].

TABLE 5 - *Positive ion masses as measured in the upper troposphere by a fragment ion mass spectrometer. Maximum fractional count rates and tentative ion identifications are also given* (after Hauck and Arnold; Ref. 29).

Mass	Percent	Ion
19 ± 2	4.3	H^+H_2O
28 ± 1	7.1	H^+A
32 ± 1	3.0	H^+B
37 ± 1	12.2	$H^+(H_2O)_2$
42 ± 2	2.0	H^+CH_3CN
50 ± 1	4.4	$H^+B \cdot H_2O$
55 ± 1	21.6	$H^+(H_2O)_3$
60 ± 1	15.8	$H^+CH_3CN \cdot H_2O$
73 ± 1	4.7	$H^+(H_2O)_4$
78 ± 1	9.0	$H^+CH_3CN(H_2O)_2$
88 ± 1	6.0	$H^+CH_3CN \cdot C$ $H^+B \cdot D$
90 ± 2	3.4	$H^+(H_2O)_5$
96 ± 2	6.8	$H^+CH_3CN(H_2O)_3$
106 ± 2	2.7	$H^+CH_3CN \cdot C \cdot H_2O$ $H^+B \cdot D \cdot H_2O$
115 ± 1	8.3	$H^+CH_3CN(H_2O)_4$
126 ± 1	5.8	$H^+(H_2O)_7$
132 ± 1	4.0	$H^+CH_3CN(H_2O)_5$
164 ± 2	1.4	$H^+B \cdot CH_3CN(H_2O)_5$
201 ± 2	2.0	$H^+(CH_3CN)_4(H_2O)_2$

A: HCN (172.7); C_2H_2 (182.6)
B: CH_3NH_2 (211.3); CH_3OH (182.2)
C: CH_2O_2 (178.1); C_2H_6O (187.0); $(CH_3)_2NH$ (225.3)
D: CH_3CHCO (200.0)

Another important tropospheric trace gas which should be detectable via ion composition measurements is ammonia. It reacts, as already mentioned, with positive ions yielding NH_4 cores. So far, however, such cores could not be detected in the upper troposphere which sets an upper limit to the ammonia vapour abundance (mole fraction) of only about $2 \cdot 10^{-12}$ around the tropopause [29].

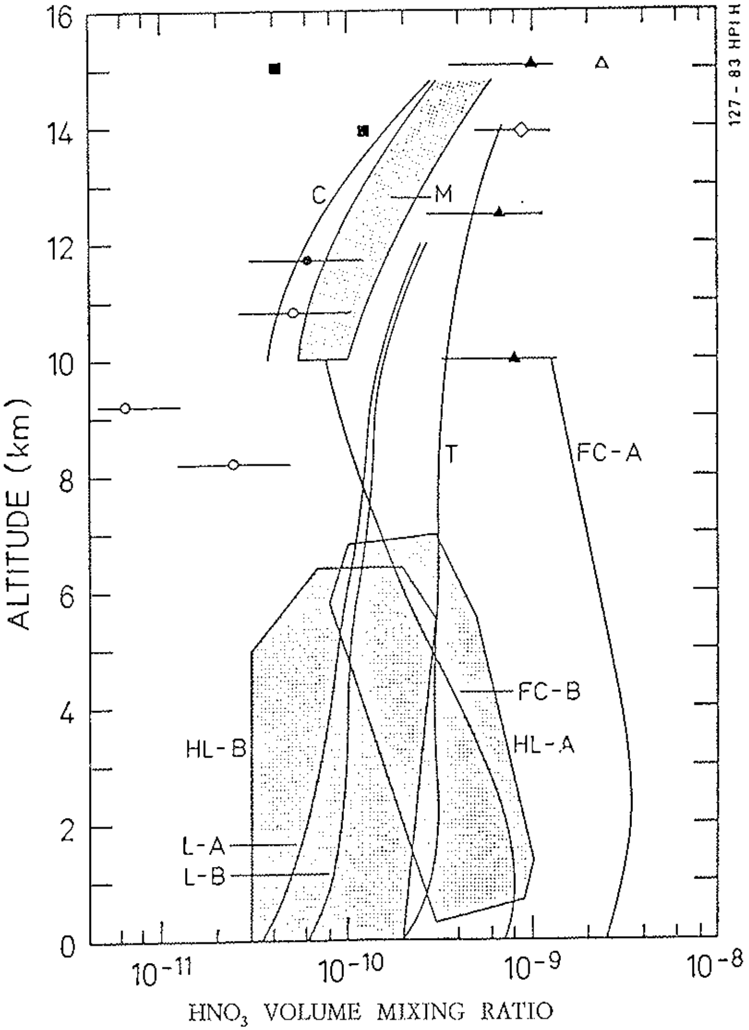

FIG. 12. Nitric acid vapour abundances as inferred from negative ion composition data (circles). Comparison is made with other measurements (symbols) and various model predictions (lines). [After Heitmann and Arnold; Ref. 12].

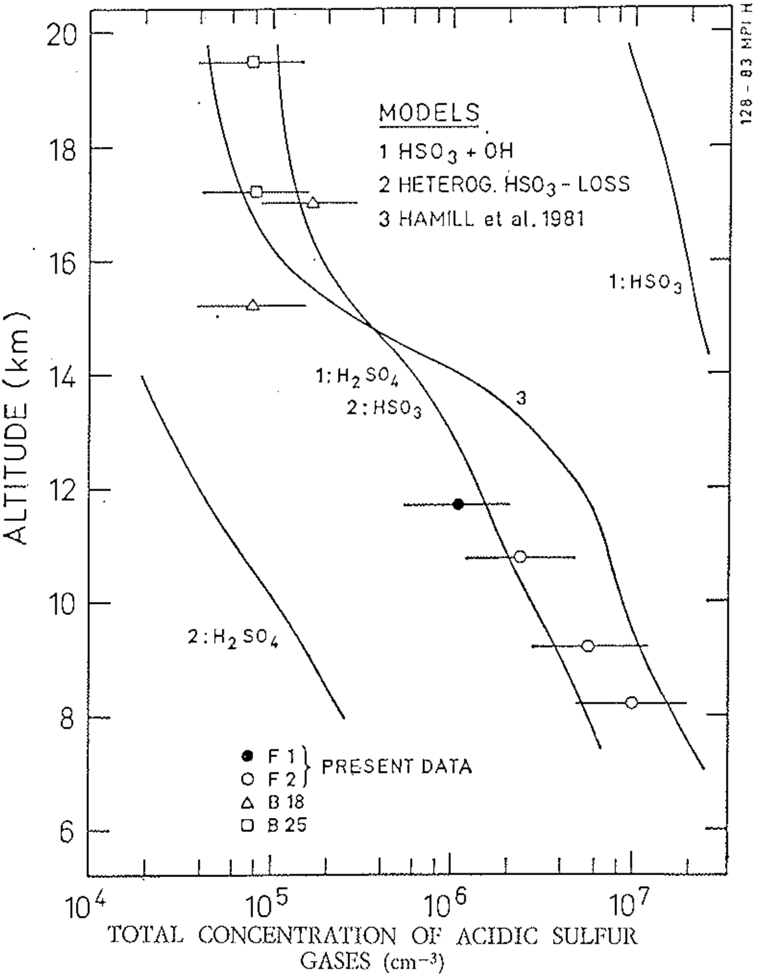

FIG. 13. Total abundances of acidic sulfur gases as inferred from negative ion composition measurements (circles). Comparison is made with model predictions (lines). [After Heitmann and Arnold; Ref. 12].

Now a possible role of free ions in tropospheric trace gas and aerosol processes will be discussed.

As far as aerosol formation is concerned, conventional ion nucleation (IN) which requires relatively large supersaturation ratios ($S \gtrsim 4$) is probably inefficient. Due to the relatively large tropospheric aerosol content, large S values can hardly build up but supersaturated vapors should condense on preexisting aerosols. Polyion nucleation may be operative but it is not known whether small polyions can grow to condensation nuclei sizes before they are scavenged by preexisting aerosols.

Concerning a possible role of ions in tropospheric trace gas processes little can be said at present. Besides ion-molecule reactions, ion-ion recombination and ion-catalyzed reactions may in this respect be important. The latter may also include "quasi liquid phase reactions" occurring in relatively large cluster ions or polyions. Maximum rates for trace gas destruction and formation are similar to those estimated for the stratosphere (see section on Potential Role of Ions in Stratospheric Trace Gas and Aerosol Processes).

As in the stratosphere, in situ ion composition measurements should offer an enormous potential for neutral trace gas detection. Likely candidates for PACIMS trace gas detection are the reactant trace gases discussed above. Diagnostic applications for probing aerosol properties also seem promising. Since tropospheric cluster ions are relatively large, they should resemble aerosol solution droplets.

ACKNOWLEDGEMENTS

Stimulating discussions with E.E. Ferguson, R. Turco, P.J. Crutzen, D.H. Ehhalt, and B. Keesee are acknowledged.

REFERENCES

[1] ARNOLD F., *Physics and chemistry of atmospheric ions.* Proc. Dahlem Workshop on Atmospheric Chemistry. Ed. E.D. Goldberg, 273-300 (1982).

[2] ARNOLD F. and FABIAN R., *First measurements of gas phase sulfuric acid in the stratosphere.* « Nature », *283*, 55 (1980).

[3] ARNOLD F., FABIAN R. and JOOS W., *Measurements of the height variation of sulfuric acid vapor concentrations in the stratosphere.* « Geophys Res. Lett. », *8*, 293 (1981).

[4] VIGGIANO A. and ARNOLD F., *Extended sulfuric acid vapor concentration measurements in the stratosphere.* « Geophys. Res. Lett. », *8*, 583 (1981).

[5] VIGGIANO A. and ARNOLD F., *The first height measurements of the negative ion composition of the stratosphere.* « Planet. Space Sci. », *29*, 895 (1981).

[6] VIGGIANO A., SCHLAGER H. and ARNOLD F., *Stratospheric negative ions - Detailed height profiles.* « Planet. Space Sci. », *31*, 813 (1983).

[7] VIGGIANO A. and ARNOLD F., *Stratospheric sulfuric acid vapor: New and updated measurements.* « J. Geophys. Res. », *88*, 1457 (1983).

[8] ARIJS E., NEVEJANS D., FREDERICK P. and INGELS J., *Negative ion composition measurements in the stratosphere.* « Geophys. Res. Lett. », *81*, 121 (1981).

[9] ARIJS E., NEVEJANS D., FREDERICK P. and INGELS J., *Stratospheric negative ion composition measurements, ion abundances and related trace gas detection.* « J. Atmos. Terr. Phys. », *44*, 681 (1982).

[10] ARIJS E., NEVEJANS D., INGELS J. and FREDERICK P., *Sulfuric acid vapour derivations from negative ion composition data between 25 and 34 km.* « Geophys. Res. Lett. », *10*, 329 (1983).

[11] ARNOLD F., *Middle atmosphere ionized component.* Proc. ESA-PAC Symposium on European Rocket & Balloon Programmes and Related Research, Bournemouth (UK) 14-18 April 1980; ESA *SP-152*, 479 (1980).

[12] HEITMANN H. and ARNOLD F., *Composition measurements of tropospheric ions.* « Nature », *306*, 747 (1983).

[13] FERGUSON E.E., FEHSENFELD F.C. and ALBRITTON D.L., *Ion chemistry of the earth's atmosphere.* In: « Gas Phase Chemistry ». Ed. M.T. Bowers, Academic Press, Inc., 1979.

[14] FERGUSON E.E. and ARNOLD F., *Ion chemistry of the stratosphere.* « Accounts Chem. Res. », *14*, 327 (1981).

[15] YOUNG J.M., JOHNSON C.Y. and HOLMES J.C., *Positive ion composition of a temperate-latitude sporadic E layer as observed during a rocket flight.* « J. Geophys. Res. », *72*, 1473 (1967).

[16] HOLMES J.C., JOHNSON C.Y. and YOUNG J.M., *Ionospheric chemistry.* « Space Res. », *5*, 756 (1965).

[17] ARNOLD F., BERTHOLD W., BETZ B., LÄMMERZAHL P. and ZÄHRINGER J., *Mass spectrometer measurements of positive ions and neutral gases between 100 and 233 km above Andoya, Norway.* « Space Res. », *9*, 256 (1969).

[18] NARCISI R.S. and BAILEY A.D., *Mass spectrometric measurements of positive ions at altitudes from 64 to 112 kilometers.* « J. Geophys. Res. », *70*, 3687 (1965).

[19] ARNOLD F., KISSEL J., WIEDER H. and ZÄHRINGER J., *Negative ions in the lower ionosphere: A mass spectrometric measurement.* « J. Atmos. Terr. Phys. », *33*, 1669 (1971).

[20] NARCISI R.S., BAILEY A.D., DELLA LUCA L., SHERMAN C. and THOMAS D.M., *Mass spectrometric measurements of negative ions in the D- and lower E-regions.* « J. Atmos. Terr. Phys. », *33*, 1147 (1971).

[21] ARNOLD F. and HENSCHEN G., *First mass analysis of stratospheric negative ions.* « Nature », *257*, 521 (1978).

[22] ARNOLD F., BÖHRINGER H. and HENSCHEN G., *Composition measurements of stratospheric positive ions.* « Geophys. Res. Lett. », *5*, 653 (1978).

[23] ARIJS E., NEVEJANS D and INGELS J., *Unambiguous mass determination of major stratospheric positive ions.* « Nature »,, *288*, 684 (1980).

[24] ARIJS E., NEVEJANS D., INGELS J. and FREDERICK P., *Negative ion composition and sulfuric acid vapor in the upper stratosphere.* « Planet. Space Sci. », (1983).

[25] ARIJS E., NEVEJANS D. and INGELS J., *Positive ion composition measurements and acetonitrile in the upper stratosphere.* « Nature », *303*, 314 (1983).

[26] QIU S. and ARNOLD F., *Stratospheric in situ measurements of* H_2SO_4 *and* HSO_3 *vapors during a volcanically active period.* « Space Sci. », *32*, 87 (1984).

[27] ARNOLD F. and QIU S., *Upper stratosphere negative ion composition measurements and inferred trace gas abundances.* « Planet. Space Sci. », *32*, 169 (1984).

[28] ARNOLD F., HEITMANN H. and OBERFRANK K., *First tropospheric ion composition measurements*: I. *Positive ions.* « Planet. Space Sci. » (1984) in press.

[29] HAUCK G. and ARNOLD F., *Positive ion composition measurements in the upper troposphere - Implications for acetonitrile and ammonia vapours.* « Nature » (1984) submitted.

[30] ARNOLD F. and HAUCK G., *Improved negative ion composition measurements in the upper troposphere.* « Nature » (1984) submitted.

[31] PFEILSTICKER K. and ARNOLD F., Unpublished material.

[32] WEBBER W., *The production of free electrons in the ionospheric D-layer by solar and galactic cosmic rays and the resultant absorption of radiowaves.* « J. Geophys. Res. », *67*, 5091 (1962).

[33] SMITH D., ADAMS N.G. and ALGE E., *Ion-ion mutual neutralization and ion-neutralization and ion-neutral switching reactions of some stratospheric ions.* « Planet. Space Sci. », *29*, 449 (1981).

[34] BATES D.R., *Recombination of small ions in the troposphere and lower stratosphere.* « Planet. Space Sci », (1983).

[35] ROSEN J.M. and HOFMANN D.J., *Balloon-borne measurements of the small ion concentration.* « J. Geophys. Res. », *86*, 7399 (1981).

[36] TURCO R.P., WHITTEN R.C. and TOON O.B., *Stratospheric aerosols: Observation and theory.* « Rev. Geophys. Space Phys. », *20*, 233 (1982).

[37] FERGUSON E.E. and ARNOLD F., *Ion chemistry of the stratosphere.* « Acc. Chem. Res. », *14*, 327 (1981).

[38] CASTLEMAN Jr. A.W., *Nucleation and molecular clustering about ions.* In: « Advanced Colloid and Interface Science », « Nucleation ». Ed. A. Zettelmoyer, 73-128. Amsterdam Elsevier Press, 1979.

[39] ARNOLD F., *Ion nucleation, a potential source for stratospheric aerosols.* « Nature », *299*, 134 (1982).

[40] ROWE B.R., VIGGIANO A.A., FEHSENFELD F.C., FAHEY D.W. and FERGUSON E.E., *Reaction between neutrals clustered to ions.* « J. Chem. Phys. », *76*, 742 (1982).

[41] Böhringer H. and Arnold F., *Acetonitrile in the stratosphere - Implications from laboratory studies.* « Nature », *290*, 321 (1981).

[42] Arnold F., *Multi-ion complexes in the stratosphere - Implications for trace gases and aerosol.* « Nature », *284*, 610 (1980).

[43] Henschen G. and Arnold F., *Extended positive ion composition measurements in the stratosphere - Implications for neutral trace gases.* « Geophys. Res. Lett. », *8*, 999 (1981).

[44] Schlager H., Fabian R. and Arnold F., *A new cluster ion ion source / ion drift cell apparatus for atmospheric ion studies - First mobility and reaction rate coefficient measurements.* In Proc. 3rd Intern. Swarm Seminar, 3-5 Aug. 1983, Innsbruck, 257-262 (1983).

[45] Ferguson E.E., *Sodium hydroxide ions in the stratosphere.* « Geophys. Res. Lett. », *5*, 1035 (1978).

[46] Perry R.A., Rowe B.R., Viggiano A.A., Albritton D.L., Ferguson E.E. and Fehsenfeld F.C., *Laboratory measurements of stratospheric sodium ion reactions.* « Geophys. Res. Lett. », *7*, 693 (1980).

[47] Arnold F. and Henschen G., *Positive ion composition measurements in the upper stratosphere - Evidence for an unknown aerosol component.* « Planet. Space Sci. », *30*, 101 (1982).

[48] Arnold F., Henschen G. and Ferguson E.E., *Mass spectrometric measurements of fractional ion abundances in the stratosphere. I. Positive ions.* « Planet. Space Sci. », *29*, 185 (1981).

[49] Brasseur G. and Arijs E., *Acetonitrile in the atmosphere.* « Geophys. Res. Lett. », *8*, 725 (1983).

[50] Crutzen P., private communication, 1983.

[51] Albritton D.L., *Ion-neutral reaction rate constants measured in flow reactors through 1977.* In: « Atomic Data and Nuclear Tables », Vol. 22, No. 1. New York, Academic Press, 1978.

[52] McCrumb J.L. and Arnold F., *High-sensitivity detection of negative ions in the stratosphere.* « Nature », *294*, 136 (1981).

[53] Arnold F., Viggiano A.A. and Schlager H., *Detection of large negative cluster ions in the stratosphere - Implications for trace gases and aerosols.* « Nature », *297*, 1 (1982).

[54] Viggiano A.A. and Arnold F., *The first height variation measurements of the negative ion composition of the stratosphere.* « Planet. Space Sci. », *29*, 895 (1981).

[55] Crutzen P., *The possible role of CSO for the sulfate layer of the stratosphere.* « J. Geophys. Res. », *3*, 73 (1976).

[56] Arnold F. *et al.*, *Annual Report of the Max-Planck-Institut für Kernphysik,* Heidelberg, 1983.

[57] Arnold F. *et al.*, *Annual Report of the Max-Planck-Institut für Kernphysik,* Heidelberg, 1982.

[58] Turco R.P., Toon O.B., Hamill P. and Whitten R.C., *Effects of meteoric debris on stratospheric aerosols and gases.* « J. Geophys. Res. », *86*, 1113 (1981).

[59] Bohme D.K., Mackay G.I. and Tanner S.D., *An experimental study of the gas phase kinetics of reactions with hydrated* H_3O^+ *ions* (n=1−3) *at* 298 K. « J. Amer. Chem. Soc. », in the press.

[60] Mühleisen R., *Atmosphärische Elektrizität.* In: Handbuch der Physik, Vol. XLVIII, p. 541. Springer-Verlag, Heidelberg, 1957.

DISCUSSION

Liberti

Will you please give us some details about how you make the sampling. Since most measurements are made in the stratosphere, I presume this has been done by aircraft. Now, and since you have been using as experimental device a mass spectrometer, how are you able to make a distinction between ions and molecules? And the second question: if the species you describe in your slides have been really shown, in other words have been experimentally demonstrated with this pathway which you assume that the ions are recombined.

Arnold

Let me answer the first question first. The sampling is essentially similar for the various ridges and also it is a little bit optimized for the specific conditions prevailing in the different layers of the atmosphere. Of course the rocket sampling will be different from the aircraft sampling. In the case of the rocket you form a molecular beam by a skimmer, this conically shaped sampling electrode, the gas approaches this skimmer under an angle of zero degrees with respect to the skimmer axis, so you sweep out a cone and you form a molecular beam, and you take care that this molecule beam is not scattered inside by freezing it out directly. So there is no dramatic disturbance of the molecular beam inside the instrument because you have raised it out . . . liquid neon or liquid helium temperature on the cold surface. And from this molecular beam you extract the ions by means of electric fields, focus them and inject them into an electric mass filter. That is in brief the technique used in the case of the rocket experiments. For balloon and aircraft measurements the sampling is somewhat different. I do not want to discuss this in detail, unless you would like it; but I may just draw your attention to a major problem of this ion sampling, which is condition-induced fragmentation. That means while you employ the electric field you will increase the condition energy of the ions with regard to the background gas, and this causes internal excitation, and dissociation of ligand molecules. We have investigated this problem in great detail in the laboratory in simulation type experiments, and we found that in fact dissociation takes place but it is not as dramatic as one may expect. Usually only one ligand is dissociated under most of the sampling conditions encountered. At the lower heights there is an additional problem: adiabatic cooling, due to adiabatic expansion, and one has to be very careful. But the main effect of this adiabatic cooling would be additional clustering of water vapor. Except you are particularly interested in the water cluster distribution, this would not hurt too much because you know essentially the only molecular species which can cluster to the ion in the adiabatically expanding gas jet would be water vapor under typical atmosphere conditions. It turns out that the opposite effect of dissociation is even stronger, so this is over-compensated by the electric field. It means you dissociate more ligands than you can add under these sampling conditions we are encountering.

About your second question, we measure plus lines (or ions) of a certain mass charge ratio, and of course we are confronted with a problem of identifying these species and the larger they are the larger the masses are, the more difficult this job gets, so you need additional information. One additional piece of information which is of experimental nature is the collisionally induced dissociation. You can dissociate the clusters stepwise, strip off the ligands in the experiment in the atmosphere by changing electric field conditions, and then you can measure fragment ion patterns. And this helps quite a lot as you may imagine.

BROSSET

This makes clear the question of sulphate, but do you agree that nitric acid has a quite different problem?

ARNOLD

There has been discussion of the possibility of a ternary aerosol system in the stratosphere involving also nitric acid besides sulphuric acid and water. This has been published several years ago in *Nature*; as far as I remember, the paper was not quite conclusive about this point. There is still a possibility that nitric acid might be involved in stratospheric aerosol. I may just briefly mention a finding from the ion cluster studies. I mentioned before that the sulphuric acid clusters containing, or carrying a negative charge are easily hydrated under atmospheric conditions, and that the degree of hydration, interestingly, increases with the size of the cluster, which cannot be explained by a pure electrostatic interaction between the so-called core ion and the water ligand. Interestingly, we found a similar behavior also for nitric acid clusters which contain an NO^- core; and both these behaviors we found first in the atmospheric data and then went back to the laboratory, produced these ions in high pressure ion sources, studied the hydration and we have at least half quantitatively reproduced the increase of hydration efficiently.

BROSSET

But in fact the drop of activity of sulphuric acid with additional water is much more than the drop of nitric acid because in rather dilute solution we have an appreciable pressure of nitric acid.

ARNOLD

I agree.

CANUTO

Just an information: do you know if any of these chains of reaction that you studied have been used by those who study the composition of comets because they have a type of reaction in cometary physics that reminds me very closely of what you are doing. Since you have direct data, you have no comparison if your reaction is reliable or not. That would be most useful to check with people who have spent their lives trying to make sense out of the data out of cometary nuclei.

ARNOLD

In fact the method may be strong in getting information on neutrons in comets, and in fact at our laboratory a mass spectrometer probe for the cometary mission of Halley's comet is prepared. But the scenario is a little bit different. Of course the gas tail of the comet has a very complex chemistry and you have gradients in concentrations and change in direction with the radiation field, that the ultimate goal would be to trace back the so-called OH. In order to get these, of course you have to translate or to unravel the entire chemistry — you measure a gas constituent which was produced by possibly not very well known processes. You have to evaporate first the material from the comet, then it is exposed to the UV radiation field of the sun, it's processed photochemically, it may undergo some reactions, so that would be very difficult. But there is a chance to get some information.

CRUTZEN

Is there a possibility that SO_2 can directly react with the clusters? You mentioned too that at some point H_2O may be also involved. If anything like that happens, then this may become very interesting.

ARNOLD

In fact this has been measured. One measurement of this kind was mentioned in the morning's talk on the quantum chemistry, namely that SO_2 reacts with NO^-_2. We have heard that this is a particularly strong bonding, and we have heard that this must be due to some additional bonding mechanism which cannot simply be explained by the bipolar charge induced by polar interaction which shows that NO^-_3 bonds very strongly to SO_2. There is the indication that the SO_2, molecule at least clusters very efficiently to negative ions but only to the small ones, to the NO^-_2, NO^-_3 ions. We have recently tried to find out if also larger negative ion clusters attach to SO_2 without any positive results.

CRUTZEN

And what about H_2O_2 You mentioned that also in your talk.

ARNOLD

This has also been measured at the NOAA lab, and it was found that H_2O_2 bonds very strongly to NO^-_3, and we make use of this reaction in trying to measure the H_2O_2. What we do is the following: we mesaure the NO^-_3 ion in the stratosphere by mass spectro in the more or less undisturbed environment. The flow or the resonance time is about 1". The flow is simply due to a relative motion of the balloon gondola with respect to the surrounding atmosphere. So this is a kind of a flow reactor experiment; and since H_2O_2 should be there, it should attach to the NO^-_3 ion. The advantage of this active method is that only small ions are involved which are known to attach to H_2O_2, whereas by contrast the natural atmospheric ions grow much larger in a time scale during which they have no chance to collide with an H_2O_2. So we hope this way to get H_2O_2 measurements in the stratosphere.

PULLMAN

You mentioned that SO_2 binds to NO^-_2 and NO^-_3 but not to larger negative ions. What larger negative ions?

ARNOLD

Well, we were naturally interested in those negative ions which are the most abundant ones in some parts of the stratosphere, as well as the NO^-_3 with two nitric acid ligands. I may mention just very briefly why we were interested in that. One may not necessarily expect SO_2 to cluster with these larger ions, but we have observed an increase of an ion which may be interpretative in terms of SO_2 clustering to nitric acid clusters in the stratospheric eruption cloud of the volcanos. If this ion does not contain SO_2 the missing ligand must be nitric acid, which has a mass number which is just one a.m.w. from the SO_2. The measurements would probably indicate that there was a marked enhancement of nitric acid vapor concentration in the eruption cloud and that could be of interest.

PULLMAN

This is just a clarification for my information. Could you give me the words for PCIMS what does it stand for?

ARNOLD

Passive chemical ionization mass spectrology. It is the term used for chemical ionization. First of all we invented the term: passive because we were using already existing natural ions, and then after we employed this method by which we formed ions in the atmosphere and we measured them.

ANDERSON

Two questions: the first, do you see any correlation between the nitric acid observations and the local water vapor concentration? Secondly, what is the altitude resolution of the method for nitric acid?

ARNOLD

Let me answer the second question first. The altitude resolution at present can be as small as of the order of 100 meters. Usually we scan the entire mass spectrum, but we could focus only on those ions which are needed in order to infer the nitric acid vapor concentration, that means we gain time, and that means we get sufficiently good ion counting statistics in a shorter time scale, and that means we can improve resolution even below 100 meters.

And the first question was if we find correlations between the nitric acid vapor content and the water vapor. To which hydrogen are you referring?

ANDERSON

To the H_2O.

ARNOLD

We do not measure water vapor directly in the stratosphere. Again we can possibly infer it from the hydrate ion distribution, but this is more difficult because here you have to rely on a thermodynamic equilibrium distribution, which can be altered due to the electric field. Therefore we feel that this method is not very useful because there exist better methods for measuring water vapor. Therefore I simply cannot argue the question. There are no parallel water vapor measurements. As far as the troposphere is concerned, the dew point is measured on the earth in parallel to the nitric acid measurements. But here, as you have seen, we have only so far obtained four data points and that would be premature to discuss anything.

HOWARD

How confident are you of the identification of the HSO_3 particle in a particular distance in the stratosphere?

ARNOLD

The HSO_3 molecule, or the molecule X which we tentatively identify as HSO_3, is clustered to the negative ions which contain also sulphuric acid molecules. And now there are two possibilities, or this additional information in order to get more than only the mass number. The mass number has been pinched down unambiguously — it is 81 atomic mass units. Unfortunately the same mass number would apply to an adduct nitric acid and water. And this is one of the problems: how to distinguish between the two possibilities. There could be mixed clusters which contain nitric acid besides the sulphuric acid and water in addition. If we accelerate these ions in an electric field we get a product which is usually an ion smaller by 81 atomic mass units, and not by 18 or 63, which would correspond to fragments of the nitric acid in the water complex. However, we cannot absolutely exclude the possibility of for instance nitric acid and water being contained in this system, and it would be very helpful to have accompanying laboratory measurements of this system — not of the HSO_3 system. That may be very tough in the laboratory, but at least the nitric acid-water-sulphuric acid mix could certainly be studied with the methods available at your laboratory.

MALONE

Have you been able to examine the distribution and mobility of ions in relation to the potential gradient which is related to the many lightning discharges daily?

ARNOLD

We have done no mobility measurements in the atmosphere. We have done mobility measurements in the laboratory, using a drift tube technique and we have studied the mobility of the major ion clusters which we find in the atmosphere, including also these recently observed sulphuric acid clusters, and one can then use these laboratory data in order to calculate the mobility on the basis of the in situ ion composition measurements. It seems that usually the average mobilities are consistent with mobility measurements made by Rosen and Hoffmann using modern techniques. But there may be one thing which might be interesting to know in this regard. The recent tropospheric measurements which we made revealed the presence of thin layers of very massive cluster ions. In other words, while you are scanning the altitude range, you find more or less ions which fit usual average mobilities. But you also find thin layers where there are very massive ions, even so massive that they appear to fall outside the mass range of the instrument, which is 800 atomic mass units.

WANDIGA

It was interesting to note some of the neutral molecules you were able to detect; but your missing some of the ones that one would expect is also striking, like the freons. Can you give an explanation for that?

ARNOLD

Well, they are interesting, but unfortunately they are not very favorable particles for reactions. They react with ions but they do not lead to stable ions. The product ions are further converted to those ions which we have seen in the compilation. And this has already been shown by laboratory measurements, particularly at the NOAA Laboratory, but unfortunately the freons which would be of interest are not good candidates for this method.