

nulling would still be observed, but not the third component. Although a null involves the entire polar cap, its causal mechanism may be confined to the centre and, therefore, seldom seen. Interestingly, in several pulsars Backer<sup>5</sup> has found modulations of typically 100 periods in addition to the short-term drift periodicities. Their possible connection with nulls does not seem to have been investigated.

Multiply-peaked integrated profiles are not uncommon among pulsars<sup>10</sup>, often with asymmetrically distributed peaks. PSR0329+54 and PSR2045-16 are perhaps the best and brightest examples. Intriguingly the binary pulsar<sup>21</sup>, whose individual pulses are too faint to detect, has also an asymmetric triple peak profile. It would, however, be rash to extend the present model to other pulsars without further investigation. The pulsars still have much to teach us, and have hidden their secrets well.

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## Unambiguous mass determination of major stratospheric positive ions

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There has been recent considerable interest in the stratospheric ion composition and ion chemistry, especially in view of its possible impact on aerosol formation<sup>1,2</sup> and the possibility of detection of minor constituents with very low concentrations<sup>3,4</sup>. The first composition measurements of positive ions in the stratosphere conducted by a rocket-borne instrument<sup>5</sup>, revealed the existence of the theoretically predicted proton hydrates (PH)<sup>6</sup> and also of some unexpected non-proton hydrates (NPH). (Proton hydrates are primarily ions of the form  $H^+(H_2O)_n$ ). Because low altitude rocket data may be biased by shock wave effects, such as ion fragmentation, the need for balloon flights was strongly felt. In 1978, data obtained with balloon-borne instruments<sup>7-9</sup> partly confirmed and extended the rocket data. There have been several explanations<sup>1,5,7,8,10</sup> of the presence of the observed NPH, but the lack of resolution of the data means an ambiguity still exists about the exact masses of these ions. We report here the first high resolution mass spectra of positive ions in the stratosphere, at 34-km altitude, where the major mass peaks can be identified unambiguously.

The data were obtained with a balloon-borne mass spectrometer, flown on 16 June 1980 with a 100,000 m<sup>3</sup> stratospheric balloon at mid-latitude (CNES launching base at Gap-Tallard, France, 44°33'N). The instrument was launched at 20.38 UT and reached float altitude (34 km) at 22.50 UT, time at which the measurements were started. The flight lasted 8 h and thus mass spectra were obtained in both night-time and day-time conditions. Both positive and negative ions were observed. All measurements were performed at float altitude.

We concentrate here on the masses of the most abundant positive ions during night-time. The data on negative ions will be reported elsewhere.

The instrument primarily consists of a high speed cryopump, described in detail elsewhere<sup>11</sup>, in which a quadrupole mass filter is built and of the associated electronics. The stratospheric ions are sampled through a small orifice (0.2 mm diameter), drilled into a thin stainless steel flange, which can be biased with respect to the gondola (draw-in potential). They are focused into the quadrupole by an electrostatic lens. After mass filtering they reach a high gain electron multiplier, the signals of which are treated by pulse counting techniques. Between the inlet aperture and the mass filter an electron impact ion source is incorporated into the lens system. It can be put on and off by remote control and enables us to analyse the residual gas in the cryopump. Simultaneously a gas mixture of argon, krypton and xenon is injected into the mass spectrometer and an in-flight mass scale calibration is performed, using the well known mass numbers of the different Ar-Kr-Xe isotopes.

The mass spectrometer covers the mass range 0-330 AMU (at high resolution) and is microprocessor controlled. This produces a very flexible system. Several modes of operation can be called on, such as positive ion sampling, negative ion sampling and the neutral or calibration mode. The mass spectra are scanned either with a constant resolution or with a constant peak width. Most of the data for positive ions were obtained with a constant peak width ( $\Delta m$ ) of 0.9 AMU at FWHM. A higher resolution setting implies a lower transmission of the quadrupole mass filter<sup>12</sup>. Because in the constant peak width mode the resolution ( $m/\Delta m$ ) is increasing with increasing mass number ( $m$ ), the transmission of the instrument will be strongly decreased at higher mass numbers. Therefore very few counts have been observed above mass 119 in the positive ion sampling mode.

Figures 1 and 2 show typical spectra, obtained in the mass domains 50-106 and 90-146 AMU respectively. The corresponding calibration spectra produced in flight are also shown. With such spectra, obtained in different mass domains, the major ion mass peaks could be identified unambiguously after the appropriate integration time. The observed mass peaks, fitting into the formerly observed PH and NPH schemes are summarized in Table 1 together with their identification.

Mass 60 is a minor peak and is not shown in Fig. 1. It has only been observed after long integration times in a small mass domain (53-63 AMU), but it is added to Table 1 for completeness.

From Table 1, two ion series can be clearly distinguished. The first series, containing masses 55, 73 and 91 can be identified as

**Table 1** Major observed positive ion mass peaks during night-time at 34 km

Mass number (AMU)	Identification X = 41 AMU	Observed count rate (mean value counts per s)
55	H <sub>3</sub> O <sup>+</sup> (H <sub>2</sub> O) <sub>2</sub>	3.7
60	HX <sup>+</sup> (H <sub>2</sub> O)	
73	H <sub>3</sub> O <sup>+</sup> (H <sub>2</sub> O) <sub>3</sub>	20.0
78	HX <sup>+</sup> (H <sub>2</sub> O) <sub>2</sub>	5.7
91	H <sub>3</sub> O <sup>+</sup> (H <sub>2</sub> O) <sub>4</sub>	1.9
96	HX <sup>+</sup> (H <sub>2</sub> O) <sub>3</sub>	30.0
101	HX <sup>+</sup> X(H <sub>2</sub> O)	2.4
114	HX <sup>+</sup> (H <sub>2</sub> O) <sub>4</sub>	0.6
119	HX <sup>+</sup> X(H <sub>2</sub> O) <sub>2</sub>	3.3

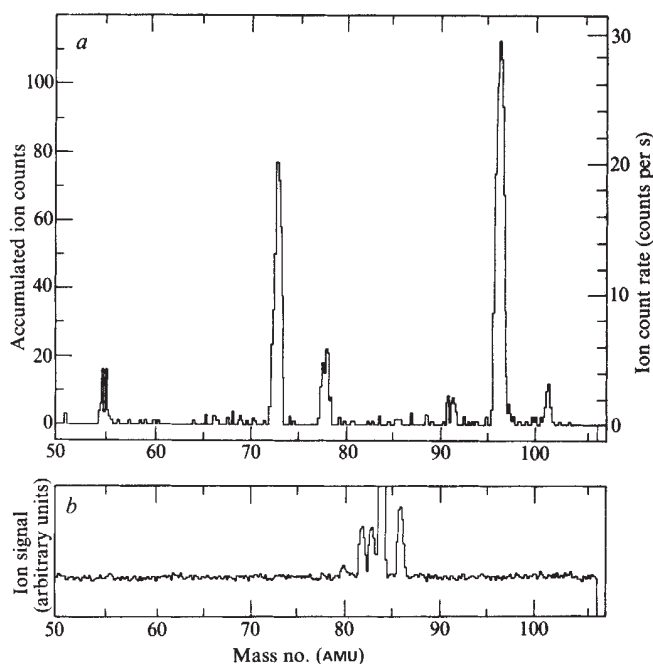
PH with the general formula  $\text{H}_3\text{O}^+ \cdot n\text{H}_2\text{O}$ . As can be expected from the thermochemical data on water ion clustering<sup>13,14</sup> mass 73 is the most abundant peak among the PH. The existence of major masses, fitting the formula  $\text{NH}_4^+ \cdot n\text{NH}_3 \cdot m\text{H}_2\text{O}$  can now be excluded from the present high resolution spectra. This confirms the conclusions about  $\text{NH}_3$  playing no significant part in the stratospheric ion chemistry at 34 km altitude<sup>8</sup>.

A second distinct ion sequence is the one containing masses 60, 78, 96, 114 and 119 AMU. It is generally accepted that these ions are the result of a reaction of the PH with an unknown trace gas X. As was suggested by the Heidelberg group<sup>8</sup> the formula of these NPH has the general form  $\text{XH}^+ \cdot n\text{X} \cdot m\text{H}_2\text{O}$ . Up to now, however, there has been ambiguity about the exact mass number of X and the best information available so far was  $41 \pm 1$  AMU.

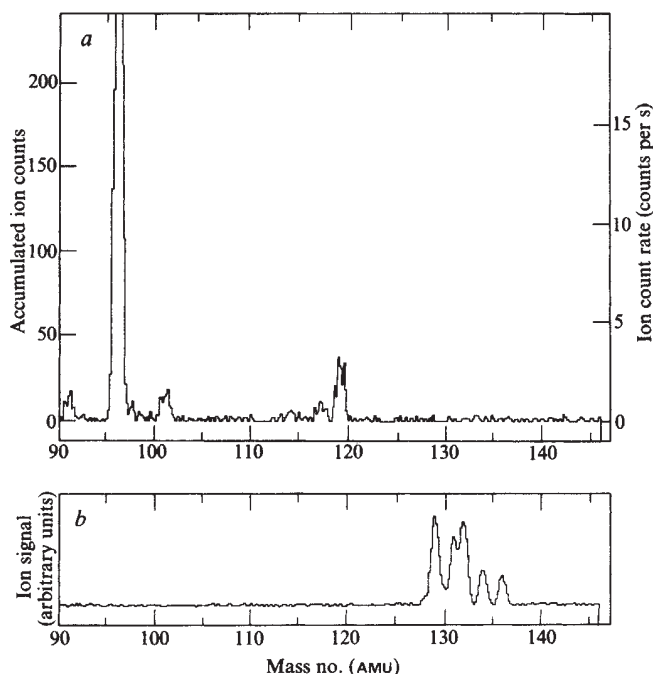
Although Arnold *et al.*<sup>5</sup> at first proposed that formaldehyde was responsible for the presence of NPH in the stratosphere, this theory was rejected after laboratory measurements<sup>15</sup>. More recently, these authors<sup>8</sup> concluded from the measured relative abundances of the PH and NPH that X must have a number density of the order of  $10^5 \text{ cm}^{-3}$  at 36 km and a proton affinity larger than  $175 \text{ kcal mol}^{-1}$ . Consequently they suggested  $\text{CH}_3\text{CN}$  (acetonitrile) as a possible candidate for X.

The fact that no formation mechanism for  $\text{CH}_3\text{CN}$  in the stratosphere was known led Ferguson to the NaOH proposal<sup>1</sup>. The existence of the sodium layer in the atmosphere<sup>16</sup> made this hypothesis quite plausible. The proposal even received support from model calculations<sup>17</sup> and laboratory work<sup>18</sup>. Recently, however, attention has been drawn to some loss mechanisms for NaOH in the stratosphere<sup>10</sup> and MgOH was suggested as a new candidate for X. However, the exact mass, as well as the identity of X has remained an open question.

The most important conclusion, which can be drawn immediately from our data, is that the mass number of the so far unknown molecule X is 41 AMU. Although mass 42 ( $\text{HX}^+$ ) has not been observed, the presence of mass 101 and 119 can only be explained by putting the mass of  $\text{X} = 41$  AMU. The conclusion rules out the hypothesis of X being NaOH (at least during night-time). The other suggestion that X might be solely MgOH is very unlikely. Actually if this were the case, one should



**Fig. 1** *a*, Typical pre-sunrise spectrum obtained in the mass region 50–106 AMU after 14 scans. Each mass unit is divided into six channels. Dwell time per channel, 0.25 s. Duration of one scan, 84 s;  $\Delta m = 0.9$  AMU FWHM. *b*, In-flight calibration obtained in the same mass domain with krypton isotopes. Only one scan is performed here.



**Fig. 2** *a*, Night-time spectrum in the mass region 90–146 AMU. Number of scans is 42. Programmed  $\Delta m = 0.9$  AMU. Real  $\Delta m$  is larger in this domain. *b*, Mass scale calibration performed in flight in the same mass domain with xenon isotopes. Result of one scan.

measure a count rate at masses 97 and 98 of  $\sim 13\%$  of that observed at mass 96, due to the isotopic abundances of  $^{25}\text{Mg}$  and  $^{26}\text{Mg}$ . This is, as Fig. 1 shows, not the case. Nevertheless, the possibility of a small contribution of MgOH to the NPH peaks cannot be ruled out completely; this will have to await high resolution data with large accumulated ion count numbers.

Most of the NPH peaks originate from a molecule with mass 41, different from MgOH. So far the most likely candidate for this molecule seems to be acetonitrile ( $\text{CH}_3\text{CN}$ ), which has a higher proton affinity than water ( $187.4 \text{ kcal}$  compared with  $168.9 \text{ kcal}$  for  $\text{H}_2\text{O}$ ) (ref. 19) as well as a higher dipole moment ( $3.92 \text{ db}$  compared with  $1.85 \text{ db}$  for  $\text{H}_2\text{O}$ ) (ref. 20). Although no production mechanism is known for  $\text{CH}_3\text{CN}$  in the stratosphere only a very low concentration ( $10^5 \text{ cm}^{-3}$ ) is required to explain the conversion from PH to NPH. In this framework a critical investigation of some neutral reactions, such as those of active nitrogen (especially in excited states), which can be produced by cosmic rays<sup>21</sup>, with  $\text{CH}_4$ , as well as ion molecule reactions of  $\text{N}^+$  and  $\text{N}_3^+$  with  $\text{CH}_4$  (ref. 22) might be useful to look for a possible source of  $\text{CH}_3\text{CN}$  in the stratosphere. Furthermore the possibility that  $\text{CH}_3\text{CN}$  (which has been observed in interstellar clouds)<sup>23</sup> originates from cosmic dust cannot be overlooked.

Note that no reaction rate coefficients for the ion molecule reaction of PH with  $\text{CH}_3\text{CN}$  have been published. Although they are exothermal and are, therefore, expected to have a large rate coefficient, the study of such reactions at the appropriate temperature is strongly recommended. Up to now, however, the only certain fact about X is its mass number and even the identification of X as acetonitrile remains speculative.

Apart from the masses listed in Table 1, a peak is observed in Fig. 2, which corresponds to 117 AMU. Although this mass can be explained by the ion  $\text{NaOH}_2^+ \cdot \text{NaOH} \cdot 2\text{H}_2\text{O}$ , it is very unlikely that it originates from NaOH because at night the other peaks of the series  $\text{NaOH}_2^+ \cdot n\text{NaOH} \cdot m\text{H}_2\text{O}$  are not observed. It is, therefore, more probable that this peak belongs to a third series  $\text{YH}^+ \cdot n\text{Y} \cdot m\text{H}_2\text{O}$ . The analysis of the minor peaks indicates the existence of other members of this family. However, a more detailed analysis of the present data, as well as high resolution mass spectra with long integration times are needed to identify this series.



Finally, note that the present data are only representative of the night-time ion chemistry at 34-km altitude and that more *in situ* measurements are needed to generalize the conclusions.

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## Carbon deposition on metallic surfaces studied by r.f. plasma discharge

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The accumulation of carbonaceous deposits on surfaces exposed to gases containing hydrocarbons or carbon monoxide is an undesirable phenomenon which can cause contamination of, for example, steel containment vessels and catalyst surfaces. It has been found<sup>1</sup> to occur also in certain conditions on the steel fuel pins of the Advanced Gas Cooled Reactor (AGR). Although in this instance it can be prevented by controlling the coolant composition, there is a strong motivation to understand the basic mechanisms involved. We show here, principally by means of a radio-frequency (r.f.) plasma-discharge system incorporating spectrographic analysis, that the deposits are formed largely as a result of the catalytic activities of the exposed surfaces (even here in the presence of highly ionized gases) and that deposition can be prevented by suitable coatings. These findings have now been confirmed by in-reactor experiments.

Whenever hydrocarbon molecules come into contact with metal surfaces, they exhibit a finite tendency to deposit carbonaceous material. This tendency depends on the chemical nature of the hydrocarbon. (For example, unsaturated molecules are particularly prone to such behaviour.) One example of this effect is the tendency for carbonaceous material to deposit on to the surfaces of the stainless steel fuel pins in an AGR. These fuel pins, which are manufactured from 20% Cr/25% Ni/Nb stabilized steel (20/25/Nb steel) are designed to operate within a temperature range 350–750 °C and be subjected to a coolant

which consists mainly of CO<sub>2</sub>, but also contains significant concentrations of CO (a few per cent) and CH<sub>4</sub> (a few hundred p.p.m. by volume). The latter component was specified to suppress any tendency for the CO<sub>2</sub> to oxidize the graphite moderator<sup>2</sup>. Although carbonaceous deposition can be prevented in practice by choosing specific levels of CO and CH<sub>4</sub> additions, it remains important to understand the basic reasons for its formation. The environment within which these events take place, namely the core of a nuclear reactor, renders direct observation very difficult, and subsequent examination of steel specimens exposed to the reactor flux is complicated by their induced radioactivity.

We have subjected specimens of the steel to an r.f. plasma discharge of a CO<sub>2</sub>/CH<sub>4</sub> gas, thereby providing an irradiation environment free from the problems of induced radioactivity. It then becomes possible to compare in laboratory conditions the amounts of carbonaceous material deposited on the steel to that deposited on other surfaces, particularly copper, which has been observed<sup>3</sup> to remain clean in reactor conditions.

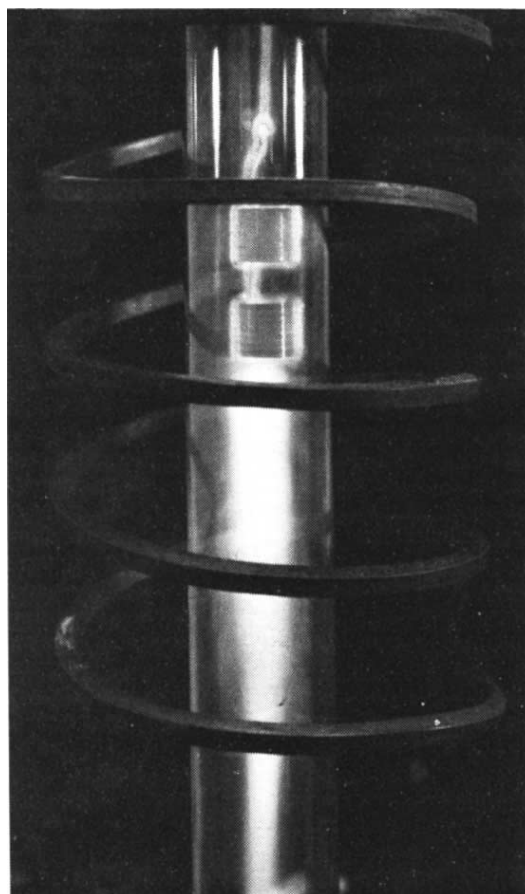


Fig. 1 Experimental arrangement showing specimens suspended in a CH<sub>4</sub>/CO<sub>2</sub> r.f. plasma discharge.

Figure 1 shows the r.f. equipment in operation. Sections of AGR 20/25/Nb steel tubing (15-mm diameter) were mounted in the middle of a silica tube, surrounded by flowing gas at a pressure of 4.7 mbar and subjected to a r.f. plasma discharge (2kV; 2.5 MHz). The gas used was an equivolument CO<sub>2</sub>/CH<sub>4</sub> mixture. This methane level is, of course, much higher than that present in an AGR but it was necessary here to counteract the enhanced oxidative capacity of the CO<sub>2</sub> induced by the intense field. In spite of this, the main effects observed previously in AGR were reproduced. Thus the steel acquired a significant deposit of carbon (0.2–0.5 mg cm<sup>-2</sup>) after 4 h, whereas speci-