In passing, it may be said that frost heaving involving $CO_2$, the major constituent of the Martian atmosphere, and probably also of the polar cap, is not a likely possibility, for the temperature and pressure conditions on Mars do not at any point lie within the liquid field of the phase diagram for $CO_2$; and, as stated above, the existence of a mobile liquid-like layer seems to be a requirement for the separation and growth of an ice lens. However, it is worth mentioning that frost heaving due to the freezing of $NH_3$ is a very real possibility on Jupiter. Spectral analysis has established that $NH_3$ is a major constituent of the Jovian atmosphere. In fact, it is thought that the thick cloud blanket of Jupiter is largely due to small crystals of $NH_3$.

Infrared radiation from the top of the cloud layer has established the temperature there to be about 130°K. Murray, Wildey, and Westphal (*11*) found that during solar eclipses the temperature observed in the 10-$\mu$ region is 185° to 196°K. They explain the temperature rise either as a decrease in opacity of the upper Jovian atmosphere due to a photosensitive reaction or a convective overturn of the atmosphere. In any case, the temperature of the lower atmosphere and on the surface must be about 190°K or possibly greater. Thus liquid $NH_3$ is possible on Jupiter (m.p. 195.4°K at 1 atm), and Glasstone (*12*) has suggested the possibility of $NH_3$ rainstorms. Given the possibility of large amounts of the liquid, fluctuating temperatures near the freezing point, and a fine-grained, porous soil, ammonia frost heaving is possible—even probable—on Jupiter.

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11 October 1966

# Composition Measurements of the Topside Ionosphere

*Abstract.* *Data from a magnetic mass spectrometer flown on the Explorer 31 satellite show that the ionosphere above 1000 kilometers usually consists of hydrogen ions as the predominant species. Between this altitude and perigee (500 kilometers) the dominant ion species shifts to atomic oxygen, with a significant amount of atomic nitrogen ions also present. Helium ions are present in small quantities at all altitudes. Other minor ions observed are those of 2, 7, 8, 15, 18, and 20 atomic mass units.*

On 29 November 1965 the Explorer 31 satellite (Direct Measurements Explorer) was launched piggyback with the Canadian Alouette II Topside Sounder from the Western Test Range. The satellites were placed in an 80° prograde, 3000-km-apogee, 500-km-perigee orbit. The Explorer 31 satellite contains experiments designed to measure directly various properties of the earth's ionosphere. This report gives some preliminary data from the magnetic mass spectrometer experiment which identifies the various positive ion species in the ionosphere and gives their relative abundances.

The instrumentation flown in this experiment consists of a small magnetic sector-field mass spectrometer. There is no ion source employed in the instrument, since it is designed to measure the relative abundances of the positive ions formed in the upper atmosphere by natural processes. The operating potentials are adjusted to permit thermal energy ambient ions to enter the mass spectrometer through an aperture in the side of the satellite. These ions then pass through the magnetic analyzer having a 1½-inch (3.8-cm) radius (the permanent magnet has a field strength of 2200 gauss) and into an electron multiplier. A 5-decade logarithmic solid-state electrometer amplifier measures the output current from the electron multiplier. The mass spectrum from 1 to 22 amu (atomic mass units) is continually swept by an exponentially decreasing voltage having a 3-second period.

Figure 1 shows a portion of an analog telemetry record taken from the satellite. A monitor of the sweep voltage is shown in the top channel and the mass spectrum appears below. The mass peaks are identified by mass number (amu). The amplitude of the peaks is given in volts, this voltage being proportional to the logarithm of the ion current detected by the electron multiplier for each ion species. This ion current is a function of the number density of that species in the vicinity of the satellite.

The satellite is oriented so that its spin axis is normal to the orbital plane. Thus, the mass spectrometer entrance aperture on the side of the satellite alternately points along the satellite velocity vector and opposite to it. Since the satellite is traveling at a speed equal to or greater than the mean velocity of the ambient ions, there is a ram and wake effect exhibited in the data as a modulation of the ion peak amplitudes. The satellite spin period is approximately 7 sweep periods. Figure 1 shows one roll-modulation cycle of data. The mass 1 peak amplitude is relatively constant while the heavy ion (mass 14, 16, 18) peaks are absent in nearly half of the spectra.

Figure 2 is a plot of the peak amplitudes of successive mass spectra as a function of time. These data were obtained from the Fort Myers, Fla., tracking station on 14 March 1966 between 1331 and 1334 GMT. The satellite altitude was 600 km at the left side and 700 km at the right side of the figure. It should be noted here that the amplitude of the roll modulation is a strong function of ion mass. For hydrogen ($H^+$), it is about 1 order of magnitude; for helium ($He^+$), 2½ orders of magnitude; and for oxygen ($O^+$), more than the 5 orders of magnitude shown in the figure. This results from the satellite velocity being large compared to the thermal velocity of the oxygen ion.

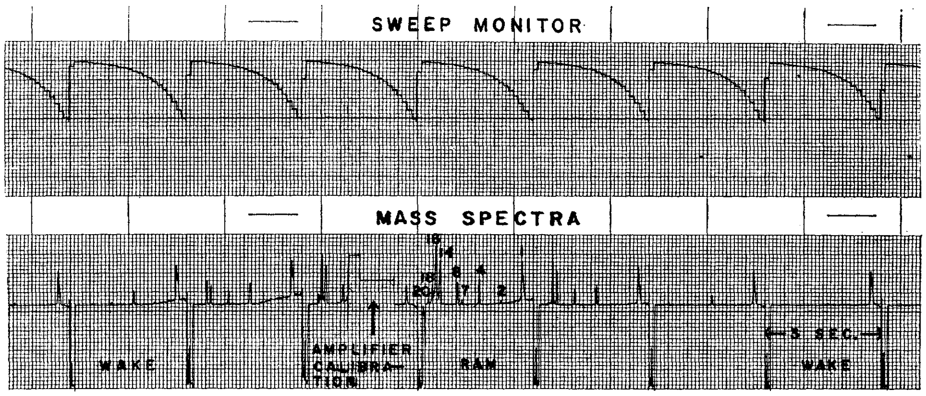

Fig. 1. Analog telemetry record for one spin period of the satellite, showing sweep monitor (top channel) and mass spectra (bottom channel). Ion peaks in mass spectrum are labeled in atomic mass units. Amplitudes are a logarithmic function of ion density. The sweep period is 3 seconds and the satellite spin period is approximately 20 seconds. Note absence of heavy mass ions (14, 16, and 18 amu) in wake positions. Internal 3-point amplifier calibration is shown on spectra channel.

Mass spectra taken when the satellite is near perigee show that the major ion peaks are at mass numbers 1, 14, and 16 (amu), while minor ion peaks occur at mass numbers 2, 4, 8, 18, and occasionally 7, 15, and 20. The peak at mass number 1 is due to atomic hydrogen ions ($H^+$); at 14, to atomic nitrogen ($N^+$); and at 16, to atomic oxygen ($O^+$). The minor ion peaks (with their mass numbers) are tentatively identified as: deuterium (2), helium (4), doubly charged oxygen (8), either water vapor or $O^{18}$ (18), neon (20), doubly charged nitrogen (7), and $N^{15}$ (15). The latter two are seen only when there is a large abundance of $N^{14}$. Doubly charged ions appear at half their mass number, since the mass spectrometer measures the mass-to-charge ratio of the ion.

The predominant ion is $O^+$ up to the order of 1000 km, where the transition with $H^+$ occurs. The transition altitude appears to vary considerably with latitude, local time, and possibly other parameters. The abundance of $N^+$ varies from 5 to 30 percent of the $O^+$, and $He^+$ is seldom more than a few percent of the total ion density. Therefore, it appears that $He^+$ is not an important constituent in the ionosphere, at least at the time these data were recorded (December 1965 to March 1966).

The mass-2 ion peak is tentatively identified as deuterium. Its roll modulation amplitude lies between that of $H^+$ and $He^+$. The mass-2 peak could also be due to doubly charged helium ions, but from the roll modulation evidence it appears that it is more likely a mass-2 particle (deuterium). However, if the satellite potential (negative) is sufficiently large the roll modulation effect cannot be used to distinguish a singly charged particle from a doubly charged one of twice the mass. The possibility of the existence of an $H^+_2$ molecular hydrogen ion at altitudes above 500 km seems unlikely. The relative abundance of the mass-2 ion varies between 1 part in $10^4$ and 1 part in $10^3$ of the mass-1 ion. The ground level abundance of deuterium is 1.5 parts in $10^4$ parts of hydrogen.

There is no evidence of a mass-3 ion peak. This peak would be due to the HD molecule or to $He^3$. The sensitivity limit of the mass spectrometer in this mass range is approximately 0.1 ion per cubic centimeter, which would represent an upper limit to the density of a mass-3 ion.

The mass-8 peak is tentatively identified as doubly charged oxygen. It is possible that this peak could be due also to $He^+_2$ (a mass-8 molecule), rather than to $O^{++}$ (a mass-16 particle), or to a combination of the two. Since a mass-7 ($N^{++}$) peak is also observed where the mass-14 ($N^+$) peak is of sufficient intensity, that is, near perigee, it is possible that at least at low altitudes the mass-8 peak could be due mainly to $O^{++}$. The mass identification is not clear from the roll modulation because the whole modulation cycle is not visible above the sensitivity limit of the mass spectrometer. Near perigee, the ratio of the mass-8 to mass-16 ion peaks is of the order of 1 percent.

As mentioned above, mass-18 could be due to either water vapor or $O^{18}$ ions, and both have been observed. For the first 2 months of the satellite life the mass-18 peak was always observed, but was not roll-modulated and had a gradually diminishing amplitude. Outgassing water vapor from the satellite is traveling at the velocity of the satellite and therefore would not be roll-modulated. After the water-vapor peak decreased sufficiently in amplitude, a roll-modulated mass-18 peak was observed, which is presumed to be the oxygen isotope at mass 18.

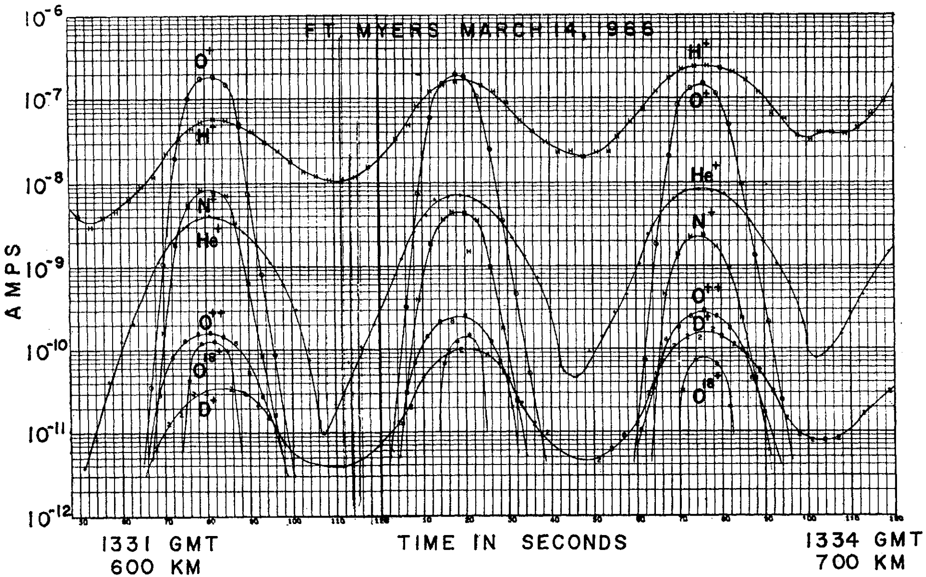

Fig. 2. Plot of peak amplitudes of successive mass spectra as a function of time, showing roll-modulation effect. Three satellite spin periods are evident. Labels of the abscissa (time in seconds) read from 50 to 120, in the left portion of the figure, and from 10 to 120 in the right portion.

A mass-15 peak is also observed, presumably due to $N^{15}+$. The heavy isotopes of nitrogen and oxygen are found in the ionic state in the upper atmosphere in abundance ratios equal to or less than those at the earth's surface.

The mass-20 peak is thought to be due to neon. The abundance of neon at the earth's surface is three times that of helium. At 900 km the $20^+/He^+$ ratio was observed to be of the order of 1 percent.

Near apogee, the mass spectra exhibit peaks only at mass 1, 2, 4, and, at times, 8 amu. Again, these peaks presumably are due to ions of hydrogen, deuterium, helium, and $O^{++}$ or $He^+_2$. The mass-18 peak was observed early in the life of the satellite, but was not roll-modulated and gradually disappeared with time as the outgassing of the satellite diminished. The predominant ion is $H^+$. The $D^+/H^+$ ratio is less than 2 parts in $10^4$, and the $He^+$ abundance is a few tenths of 1 percent. The mass-8 peak appears in this altitude region where there is no mass 16 ($O^+$). Its abundance is of the order of that of the mass-2 ion.

The experiment described is still operating normally (September 1966).

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# Deuterium Isotope Effect on Carbon Isotope Fractionation in Photosynthesis

Abstract. *Plants grown in $D_2O$ show a decreased tendency to fractionate carbon-13 during photosynthetic incorporation of carbon dioxide. The isotopic ratio $C^{13}/C^{12}$ of the tissues of deuterated plants appears to be proportional to the deuterium content of the tissue. This effect was found in specimens of the partially deuterated vascular plant* Nicotiana tabacum *as well as in cultures of the fully deuterated alga* Chlorella vulgaris.

Slight variations in the carbon isotope ratio of plant material were first noted by Nier and Gulbranson (*1*). Extensive compilations made by Wickman (*2*) and Craig (*3*) of the $C^{13}/C^{12}$ ratio in plant tissue show that all plants discriminate to the extent of a few percent against the heavy isotope of carbon during photosynthetic carbon dioxide fixation. Furthermore, different plant types within the various taxonomic groups have $C^{13}/C^{12}$ ratios that fall within rather narrow ranges. After the initial fixation of carbon dioxide, subsequent fractionations may occur in various metabolic reactions and syntheses, and some of these have been studied by Abelson and Hoering (*4*) and by Park and Epstein (*5*, *6*). Since deuterated plants have been found to show significant differences in morphology and biochemistry as compared to the same species of normal isotopic composition (*7*), it is not surprising that the patterns of isotopic fractionation may be altered in the isotopically altered organism.

Seeds of field-grown tobacco plants (*Nicotiana tabacum* L.) were germinated in water, then transferred to deuterated media when the seedlings were several centimeters high (*8*). Growth took place in well-aerated, hydroponic solutions containing only carbon-free, inorganic salts and up to 70 percent $D_2O$ in the culture media. After growth and onset of inflorescence, stems, flowers, seed parts, and leaves of various ages were desiccated in vacuum and burned in a closed system that permitted collection of the water of combustion and carbon dioxide. The deuterium fixed in the tissue was determined by infrared analysis of the collected water (*9*), and the carbon-isotope ratio was determined mass spectrometrically. Isotope ratios were determined by comparison with a local standard, then related to the Solenhofen limestone standard by a correction factor. The upper group of points in Fig. 1 shows the carbon isotope ratios for tobacco, plotted in units of δ per mil as a function of the deuterium content. The value of δ (per mil) is defined as

$$\delta = \left(\frac{C^{13}/C^{12}\ (\text{sample})}{C^{13}/C^{12}\ (\text{standard})} - 1\right) \times 10^3$$

The error in the determination of δ is estimated as ± 0.1 per mil.

The curve drawn in Fig. 1 is based on a least-squares analysis of all the points, a linear relation between deuterium content and δ value being assumed. Extrapolation of the curve to zero deuterium concentration yielded a value for the intercept of $\delta = -28$. This value is within the range found for isotopically normal vascular plants growing in atmospheric carbon dioxide, and compares well with the δ value determined for the water-grown control plants, $\delta = -28.5$. We believe the indicated slope from the least-squares analysis is real, and this is confirmed by experiments on algae, described below, in which the variables were better controlled. It should be emphasized that the scatter is a result of biological variability and is not due to analytical errors in the mass spectrometry.

The spread of the points for tobacco may be due to the grossness of the sampling technique employed and lack of control over important variables. A typical combustion sample of stem or leaf represented tissue formed during a large fraction of the lifetime of the plant, during which the deuterium content, as well as fixed-carbon content of the tissue, was continually changing in an unknown manner. Also, the isotopic makeup of material being translocated was unknown; cytoplasmic carbon dioxide has been shown to have a carbon-isotopic ratio significantly different from from that of other plant parts (*5*). Moreover, it was not possible in the experiment to correct for the carbon isotopic ratio present in tissue before transplantation of seedlings to deuter-

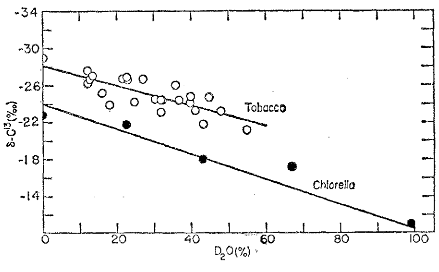

Fig. 1. Fractionation of carbon isotopes in *N. tabacum* and in *C. vulgaris* as a function of the deuterium level of the tissues. The δ values for *C. vulgaris* have been corrected to express enrichment relative to the input carbon dioxide (measured value for $\delta_{CO_2}$ in feed gas was —25.3 per mil). Tobacco plants were grown in $D_2O$ concentrations of 0, 30, 50, 60, and 70 percent $D_2O$; *Chlorella* cultures were grown in deuterium concentrations of 0, 25, 50, 75, and 99.6 percent $D_2O$.