Reports

Evidence for Chain Molecules Enriched in Carbon, Hydrogen, and Oxygen in Comet Halley

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In situ measurements of the composition and spatial distribution of heavy thermal positive ions in the coma of comet Halley were made with the heavy-ion analyzer RPA2-PICCA aboard the Giotto spacecraft. Above 50 atomic mass units an ordered series of mass peaks centered at 61, 75, 91, and 105 atomic mass units were observed. Each peak appears to be composed of three or more closely spaced masses. The abundances decrease and the dissociation rates increase smoothly with increasing mass. These observations suggest the presence of chain molecules that are enriched in carbon, oxygen, and hydrogen, such as polyoxymethylene (polymerized formaldehyde), in comet Halley.

Comets are believed to be primitive remnants of the interstellar gas and dust that condensed to form the solar system. Spectroscopic observations of the outgassed material from comet nuclei have revealed more than 20 molecular species (*1*). Most of these are unstable radicals and ions that appear to be the dissociation products of larger parent molecules. Water is the most abundant parent molecule (roughly 80% by volume). Other molecules have been detected (such as HCN, CH_3CN, H_2CO, S_2, and NH_3), but little is known about more complex parent molecules.

We report here the detection of heavy ions in the inner coma of comet Halley with mass peaks that range from 61 to at least 105 atomic mass units (amu) that are separated by 14 to 16 amu. The progressive dissociation of polyoxymethylene (POM), a linear chain of polymerized formaldehyde (. . .–CH_2–O–CH_2–O–. . .), appears consistent with the mass peak locations, widths, abundances, and dissociation rates.

The Positive Ion Cluster Composition Analyzer (PICCA), which is part of the RPA-COPERNIC plasma instrument, is one of three mass spectrometers aboard the Giotto spacecraft. The other two (*2, 3*) measured the neutral and ionic composition up to about 60 amu, whereas the PICCA covered the mass range up to 210 amu to search for the more complex molecular ions and clusters. Giotto was a fast flyby encounter with a speed relative to the Halley nucleus of 68.4 km sec^{-1}. On the inbound trajectory the spacecraft-comet-sun angle was 107°. The closest approach was at a distance of 605 km on the sunward side.

PICCA is not a true mass spectrometer in that it measures E/q (energy/charge) instead of mass. However, since the ions in the inner coma are cold (thermal velocity << ram velocity), their motion with respect to the spacecraft is highly collimated in the ram direction at the relative flyby velocity of 68.4 km sec^{-1}. Most of these ions should be singly charged so that, to zeroth order, measurements of E/q are proportional to mass.

PICCA consists of an electrostatic analyzer that was designed to provide a fixed mass resolution of 0.4 amu for 10 to 51 amu and 1 amu for 51 to 210 amu (*4*). Ions were detected with two channel electron multipliers that have different geometric factors in order to provide a large dynamic range (from approximately 0.001 to 1000 cm^{-3}). The field of view (±6° in the ram direction) was large enough to allow for ion trajectory variations due to thermal and flow velocities or spacecraft potentials or both. The spectrum integration time of 3.2 seconds was chosen to be different from the spacecraft spin period of 4 seconds to provide angular information.

The measured E/q spectra were fit with a Maxwell-Boltzmann distribution in which the composition, temperature (T), and projection of the bulk flow velocity along the ram direction (V_{f_x}) were free parameters (*5*). The detection of cold thermal ions with mass greater than ~100 amu was limited by the presence of a hot ($E/q > 2$ keV/q)-ion component of unknown composition and origin in the inner coma. However, since the maximum angular response of the detector was offset by a few degrees from the ram direction, cold ions that flowed at a small angle to the ram direction caused density oscillations as the spacecraft spun and the detector alternately looked into and out of the flow. The hot component was isotropic over the field of view so the density oscillations could be used to separate the cold and hot components.

Figure 1 shows a summed PICCA mass spectrum in the inner coma region. The mass scale is corrected for ion bulk flow velocity along the ram direction. The spacecraft potential is probably less than a few volts (*6*), which could cause a shift that is only a small fraction of an atomic mass unit, so this correction was neglected. The approximate locations of the peak centers are 61, 75, 91, and 105 amu. Density oscillations were observed from 117 to 130 amu, which revealed the presence of cold ions, although no mass peak is evident above the background. Above 130 amu, fluctuations of the hot component completely dominate any cold-ion oscillations.

The hot-ion component was subtracted in Fig. 1, and the resulting spectrum fit with the Maxwell-Boltzmann distributions of many masses. The temperature ($kT = 0.36$ eV, where k is Boltzmann's constant) was determined from the PICCA water group data by using the relative abundances of Schwenn *et al.* (*7*). This temperature was assumed to apply to all mass constituents. During the integration period of Fig. 1, Lammerzahl *et al.* (*6*) found that the ion temperatures of the water group and the ions from 26 to 35 amu were the same to within ~0.1 to 0.2 eV. The spectrum was fit with the minimum number of masses. More masses could be present, but with the assumption of equal temperatures for all ions, at least three masses over a range of ~7 amu were required to fit each mass peak.

Even when we allowed for a higher temperature, the 61-amu peak could not be fit with a single mass Gaussian, but required a minimum of three masses with $kT \leq 0.86$ eV. In order for the mass peaks at 75 and 91 amu to result from a single mass, the temperatures must be 1.55 eV and 1.37 eV, respectively—temperatures that we believe are unlikely. Furthermore, several spectra were obtained inside the contact surface (4800 km), where the water group tempera-

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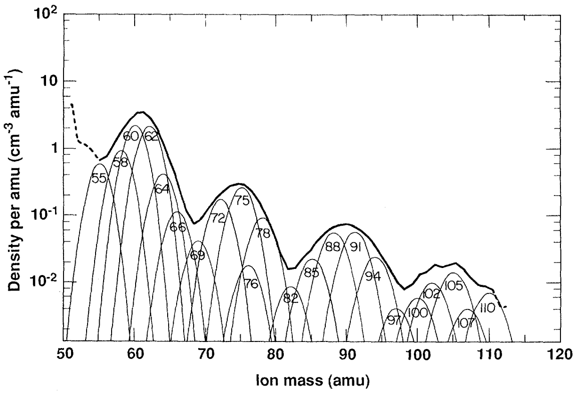

Fig. 1. Mass spectrum of the cold thermal ions in the inner coma region (9,000 to 14,000 km). The thick line is data from which a hot-ion component has been subtracted (see text). The thin lines are the Maxwell-Boltzmann distributions for the various component masses. The sum of these distributions is indistinguishable from the data between 55 and 98 amu and is within a line thickness above 98 amu.

ture dropped suddenly to $kT = 0.03$ eV (*7*). Although the hot-ion component contribution was too large inside the contact surface to allow resolution of the higher mass peaks, the 61-amu peak was clearly resolved into several masses separated by 1 to 2 amu over a range of at least 4 amu.

Figure 2 shows the radial density profiles of the mass groups indicated in Fig. 1 from a distance of 45,000 km to nearly closest approach. The C^+ curve was obtained by detailed fits to the PICCA data in the range from 10 to 24 amu. The other curves were obtained by summing the counts in each mass peak and by using the density oscillations to subtract the hot-ion component. The peak curves at 31 and 45 amu were truncated as the detector became saturated at these masses. The water group ion profile is adapted from Balsiger *et al.* (*2*) and normalized by the unsaturated PICCA data to obtain absolute density. The neutral water density (*3*) is also shown for comparison. The abundances of the mass peaks from 61 to 105 amu decrease smoothly with increasing mass. The abundance of the ions in the range from 117 to 130 amu, which was estimated from the density oscillations, is smaller by about a factor of 3 than that of the 105-amu peak. The total abundance of ions in the mass range from 61 to 120 amu relative to the water ions is 0.3%.

The number densities of C^+, neutral and ionized water, and the mass peaks at 31 and 45 amu vary approximately as r^{-2} at radial distances between 45,000 and 10,000 km. An inverse-square distance dependence corresponds to radial outflow at constant velocity with no net local production or loss. The densities of higher mass peaks generally decrease more rapidly with distance than r^{-2}. Other more rapid variations are observed in the ion densities but not in the neutral water density. Between approximately 9,000 km and 11,000 km the densities of all ion peaks increase with no corresponding increase in the neutral density. This "ion pile-up" region is discussed by Sauer and Baumgärtel (*8*). The apparent density minima at ~12,000 km in the density profiles from 75 to 105 amu, however, is probably due to a rapid change in the flow parameters that distorts the density oscillations used in the determination of density for the heavy ions. The 61-amu peak has a negligible hot-ion component and thus reflects the true density profile. For $r > 12,000$ km the density oscillations are regular for all mass peaks.

This systematic behavior of the spectrum suggests the presence of a long repeating-chain molecule that is rich in carbon, hydrogen, oxygen, and possibly nitrogen, and that can break up into shorter pieces. A 14-amu separation could be due to atomic nitrogen but is probably due to methylene (CH_2) since carbon appears to be abundant (Fig. 2) and more abundant than nitrogen (*2*). Similarly, a 16-amu separation is probably due to oxygen. The width of each mass probably results from the dissociation or attachment of one or more hydrogen atoms to unsaturated bonds on the heavy molecules.

The mass peaks at 61, 75, 91, and 105 amu dominate all heavy mass spectra obtained by the PICCA instrument. We find no evidence for a significant abundance of iron (56 amu), as reported by Gringauz *et al.* (*9*). An extrapolation of the high-mass pattern to lower masses suggests a contribution of roughly 15% to the 45-amu mass peak, which has been previously identified as CS^+, CO_2^+, HCS^+, HCO_2^+, and CH_2SH^+ (*10*).

The dissociation products of POM coincide with the observed peak locations (*11*). Modeling of the progressive dissociation of the C–O bonds of a long chain of POM results in a smooth decrease in abundance with increasing mass (*12*). Hydrogen atoms can attach to the carbon or oxygen at the open ends of the chain or be dissociated from the methylene units within the chain to provide some peak width. The observed mass spectrum (Fig. 1), however, clearly shows the presence of ions in the ranges from 63 to 67 amu and from 93 to 95 amu (assuming a temperature of $kT = 0.36$ eV) that cannot be produced by the breakup of POM. If we use an arbitrary temperature, no acceptable fit to the 61-amu mass peak can be obtained without ions beween 63 and 67 amu. Thus some other species must be present.

Since the C–O bonds of POM are identical, each bond has an equal probability of being broken, which results in a net dissociation rate that is proportional to the number of C–O bonds. On average, the dissociation of a given chain length will produce equal numbers of all shorter chain lengths. Thus dissociation of long chains acts as an extended source for shorter chains. Since the abundances of any two high-mass peaks differ by at least a factor of 3 at $r = 10^4$ km (Fig. 2), the observed loss rate of the high-mass peaks for $r = 10^4$ km should be approximately equal to the actual dissociation rates.

The average loss rates from 12,000 to 20,000 km for the 61-, 75-, and 91-amu peaks were determined by dividing the outflow velocity (assumed to be constant at 1 km sec^{-1}) by the distance over which the density multiplied by r^2 decreased by a factor of e in Fig. 2. The 105-amu loss rate was determined from 12,000 to 15,000 km and normalized to the 91-amu loss rate over the same distance range. The loss rates increase with mass (Fig. 3). If POM is the dominant constituent of the heavy ions and if dissociation of C–O bonds is the domi-

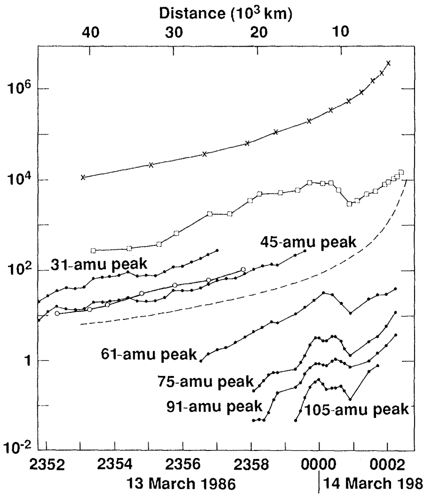

Fig. 2. Radial density profiles for the mass peaks shown in Fig. 1 as well as for the mass peaks centered at 31 and 45 amu. The mass ranges summed for each peak are as follows: 31-amu peak, 24 to 39 amu; 45-amu peak, 39 to 55 amu; 61-amu peak, 55 to 69 amu; 75-amu peak, 69 to 83 amu; 91-amu peak, 83 to 98 amu; and 105-amu peak, 98 to 114 amu. The C^+ profile (○) is obtained from detailed fits to the 10- to 24-amu range. The profiles of neutral water (x, *3*) and water group ions (□, *2*) are shown for comparison. The r^{-2} dependence is shown as a dashed line. The time scale is universal time at comet Halley.

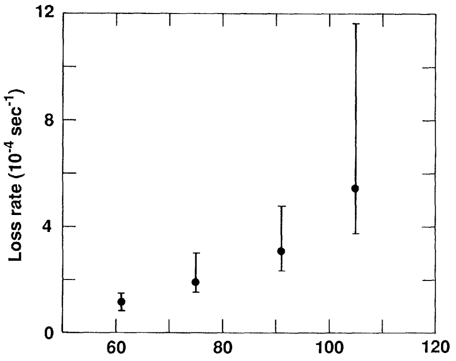

Fig. 3. Loss rates for the 61-, 75-, 91-, and 105-amu peaks from 12,000 km to 20,000 km that were determined from the density profiles in Fig. 2. The uncertainty is dominated by the ion density variations, which allow a range of exponential fits.

nant loss process, then from the data in Fig. 3 we determined that the average dissociation rate for a single C–O bond is ~5×10^{-5} sec^{-1}. This is roughly twice the water dissociation rate (*3*).

POM may be a constituent of cometary dust since it has an affinity for graphite and silicates (*11, 12*). Most of the dust particles observed in the coma of Halley are richer in carbon, nitrogen, and oxygen than are CI carbonaceous chondrites, which suggests the presence of radiation-processed ices (*13*). There is also evidence that dust particles are an extended source of CO (*14*) and also of CN (*15*) in the coma of Halley.

Cosmic ray irradiation of ices in interstellar space (*16*) can produce POM, which has been postulated to explain the broad spectral features at 10 and 18 μm of interstellar dust commonly attributed to silicates (*17*). These spectral features are also observed from comets but are found to disappear at temperatures of ~500 K. This is consistent with the vaporization temperature of POM, but not of silicates, which have vaporization temperatures >1500 K (*18*).

We estimate a mass ratio of ionized POM to dust of 2×10^{-4} at $r = 10^4$ km by assuming a dust to gas mass ratio of 0.3 (*19*) and that the peaks from 61 to 105 amu consist entirely of POM. The total POM to dust mass ratio is larger than this; however, the ionization rate and hence the ionization fraction of POM is unknown. If we assume that the ratio of POM^+ to POM is the same as the ratio of H_2O^+ to H_2O, then the mass ratio of POM to dust is ~0.02 at $r = 10^4$ km. The mass ratio of POM to dust is likely to be higher in the nuclear material since some of the POM may have dissociated into fragments with masses less than 61 amu at a distance of $r = 10^4$ km.

REFERENCES AND NOTES

1. A. H. Delsemme, *Proc. Astron. Soc. Pac.* **97**, 861 (1985).
2. H. Balsiger *et al.*, *Nature (London)* **321**, 330 (1986).
3. D. Krankowsky *et al.*, *ibid.*, p. 326.
4. A. Korth *et al.*, *J. Phys. E*, in press.
5. D. L. Mitchell *et al.*, *ESA SP-250* (European Space Agency, Paris, 1986), vol. 1, p. 203.
6. P. Lammerzahl *et al.*, *ibid.*, p. 179.
7. R. Schwenn *et al.*, *ibid.*, p. 225.
8. K. Sauer and K. Baumgärtel, *ibid.*, vol. 3, p. 401.
9. K. I. Gringauz *et al.*, *ibid.*, vol. 1, p. 93.
10. D. Krankowsky *et al.*, *ibid.*, p. 381.
11. W. F. Huebner, *Science* **237**, 628 (1987).
12. ——— *et al.*, *Proceedings of the Symposium on the Diversity and Similarity of Comets*, European Space Agency, Brussels, 6 to 9 April 1987 (European Space Agency, Paris, in press).
13. J. Kissel *et al.*, *Nature (London)* **321**, 280 (1986).
14. P. Eberhardt *et al.*, *ESA SP-250* (European Space Agency, Paris, 1986), vol. 1, p. 383.
15. M. F. A'Hearn *et al.*, *Nature (London)* **324**, 649 (1986).
16. V. I. Goldanskii, M. D. Frank-Kamenetskii, I. M. Barkalov, *Science* **182**, 1344 (1973); V. I. Goldanskii, *Sov. Phys. Dokl.* **22**, 417 (1977).
17. N. C. Wickramasinghe, *Mon. Not. R. Astron. Soc.* **170**, 11P (1975).
18. D. A. Mendis and N. C. Wickramasinghe, *Astrophys. Space Sci.* **37**, L13 (1975).
19. F. L. Whipple, *ESA SP-250* (European Space Agency, Paris, 1986), vol. 2, p. 281.
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First Polymer in Space Identified in Comet Halley

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The heavy-ion mass spectrum obtained in the inner coma of comet Halley with the PICCA instrument on the Giotto spacecraft has been examined. Short polymer chains of polyoxymethylene and their decay products are identified as the source for the spectrum with six mass peaks between about 45 and 120 atomic mass units. The properties of polyoxymethylene are consistent with many of the unexpected observations in the coma.

THE POSITIVE ION CLUSTER COMPOSITION Analyzer (PICCA) on the Giotto spacecraft detected ion masses up to about 120 atomic mass units (amu) in the coma of comet Halley (*1*). The lighter ions have a smaller radial density gradient and a much larger range in the coma than the heavy ions, which are limited to about 25,000 km. The velocity and temperature of the ions increase with increasing distance from the nucleus (*2*). Figure 1 illustrates the spectrum on which the original identification was based (*3*). The mass scale is uncorrected, but corrections are 1 amu or less. The mass spectrum is saturated below 35 amu and it is partially saturated between 43 and 46 amu. However, there is a peak at 44 or 45 amu (more probably the latter). The higher masses reveal a regular pattern: (i) Peaks with symmetrical profiles are in an alternating sequence with a separation of 14 and 16 amu up to 105 amu. (ii) The half-intensity half-width is 2 or 3 amu and is about constant from peak to peak, although it may increase slightly with increasing mass. Because of the intrinsic uncertainty associated with this width, the peak separation could also be 15 amu. (iii) The peaks show a smooth decrease of intensity with increasing mass.

The spectrum is too regular to be caused by a combination of unrelated molecular ions such as $HNCO^+$ (43 amu), CO_2^+ (44 amu), CS^+ (44 amu), HCO_2^+ (45 amu), HCS^+ (45 amu), $H_2CO_2^+$ (46 amu), H_2CS^+ (46 amu), CH_2SH^+ (47 amu), SO^+ (48 amu), $HNCS^+$ (59 amu), OCS^+ (60 amu), $HCSO^+$ (61 amu), H_2CSO^+ (62 amu), S_2^+ (64 amu), SO_2^+ (64 amu), CS_2^+ (76 amu), HCS_2^+ (77 amu), $H_2CS_2^+$ (78 amu), and so forth. It may seem possible, after initially examining the spectrum, to find uncorrelated molecular species that contain the abundant elements hydrogen, carbon, nitrogen, oxygen, and sulfur between 43 and 48 amu, but this task becomes increasingly more difficult for species at the higher mass peaks in the spectrum, which makes symmetrical profiles with a nearly constant half-intensity half-width implausible. Furthermore, an explanation would have to be found why related species with molecular masses that do not coincide with the mass spectrometer peaks, such as HSO^+ (49 amu) and C_2S^+ (56 amu), are absent or underabundant.

A rather natural explanation for the regularity of the observed spectrum emerges if its

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