

Fig. 3. Loss rates for the 61-, 75-, 91-, and 105amu 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 ${\sim}5\times10^{-5}~\text{sec}^{-1}.$ 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 $18 \ \mu m$ of interstellar dust commonly attributed to silicates (17). These spectral features are also observed from comets but are found to disappear at temperatures of \sim 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.

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First Polymer in Space Identified in Comet Halley

W. F. HUEBNER

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.

HE 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 halfintensity 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), CO₂⁺ (44 amu), CS⁺ (44 amu), HCO₂⁺ (45 amu), HCS^+ $(45 \text{ amu}), \text{ H}_2\text{CO}_2^+$ (46 amu), H₂CS⁺ (46 amu), CH₂SH⁺ (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

Southwest Research Institute, San Antonio, TX 78284.

sources are the correlated decay products of a polymer. Since all of the polymer products would have the same end-capping (that is, the same termination of the unsaturated end), the width of the spectral peaks would be about the same. The decay products are either multiples of 15 amu or alternating sums of 14 and 16 amu. The next peak in the sequence after 105 amu should be at either 120 or 121 amu. Because of the increasing intensity of a hot-ion component in the observed spectrum, the signal-tonoise ratio is too small to identify peaks above 105 amu, but when sequences are analyzed in which four mass channels are always summed into one unit and the hotion background is subtracted, then the signal-to-noise ratio is large enough so that a peak between 117 and 130 amu can be seen (4). (The unit that contains masses from 121) to 124 amu is highest in intensity.)

Because hydrogen, oxygen, carbon, and nitrogen are astrophysically the most abundant and chemically active elements, polymers that consist of these elements are the most likely to form. With the restrictions given above on abundance and mass separation, only a few polymers or oligomers are possible candidates: $(NH)_n$ and $(H_2CO)_n$. Of these, $(H_2CO)_n$ is preferred because oxygen and carbon are more abundant than nitrogen astrophysically, as well as in the coma of comet Halley. The spectra in which the mass scale has been corrected and the hot-ion component has been subtracted show the alternating differences in the mass peaks at 14 and 16 amu more clearly and also favor this interpretation (5). The chain molecule $(H_2CO)_n$ is polymerized formaldehyde, also known as polyoxymethylene (POM). POM also has physical properties that explain the presence of the six mass peaks at about 45, 61, 75, 91, 105, and 121 amu observed in the spectrum: (i) Since the C-O single bonds are symmetrical and of lower energy than the C-H bonds, impact or photo-dissociations in the coma cause POM to disintegrate easily into compounds that consist of alternating methylene (CH₂, 14 amu) and oxygen atom (16 amu) units. Subsequent ionizations allow detection of

Fig. 1. Historical heavy-ion mass spectrum from the Giotto PICCA instrument, 14 March 1986, averaged over cometocentric distances from 8,200 km to 12,600 km [courtesy of Mitchell et al. (3)]. The mass scale is uncorrected for possible flow along the ram direction. The peak from 44 to 46 amu is partially saturated and the left edge of the spectrum shows complete saturation. A hotion background component appears to dominate the cold ions beyond 105 amu.

Fig. 2. A short chain of polymerized formaldehyde $[(H_2CO)_5]$. The free ends show an affinity for graphite, silicates, and molecular species such as H, OH, CN, and their ions. Attachment of one hydrogen atom is indicated by the broken circle. The chain can be broken with nearly equal probability at any C-O bond.



Figure 2 shows a short chain of POM with one hydrogen atom attached at one of the unsaturated ends (broken circle). Because atomic hydrogen is abundant in the coma, it is the most likely species to bond to POM. Other species that are abundant in the coma gas, such as OH, H⁺, OH⁺, and CN, may also bond. The typical binding energy of a single C-O bond is 3.8 eV. The binding energy will be somewhat lower near the center of the polymer than near the end positions and is always less than the 4.5-eV binding energy of a typical C-H bond. Polarizability and cross sections of a molecule increase with its length. Progressive dissociation of any of the symmetric single C-O bonds is likely to produce the spectrum presented in Fig. 1. For example, (H₂CO)₅ may produce alternatively in one dissociation, with no rearrangement, $(H_2CO)_4 \cdot CH_2 + O,$ $(H_2CO)_4 \cdot O + CH_2,$ $(H_2CO)_3 + (H_2CO)_2$, and $(H_2CO)_2 \cdot H_2C +$ (H₂CO)₂·O (the center dots in these structures indicate a one-electron bond). Each of



these can be dissociated further in successive steps. Thus the heavy components are primarily dissociated, whereas the light species are at first formed and then progressively dissociated until they are finally dissociated into atomic species. Some molecular rearrangements of the decay products may occur and produce isomers such as alcohols, ethers, aldehydes, and olefins. However, these would not be identifiable as different species in the PICCA instrument. Radiative degradation of polymers, with a very brief comment about POM, has been summarized by Shalaby (6).

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Ionization of the various products by photons, charge exchange, electron impacts, and ion reactions (primarily protonization) makes them detectable in the PICCA instrument. Charge exchange and protonization reactions are particularly fast for large molecules because of their high polarizability (7). Dissociative electron recombination is very effective in the destruction of the heavy ions. Successive dissociations account for the large radial gradient of the heavy species in the coma, whereas the lighter species will have a smaller gradient and larger range. The lighter products will also have a higher temperature and larger velocity. The tentative identification of the monomer H₂CO in comet Halley in the infrared and radio spectrum (8) is consistent with unzippering of POM. POM may also be the extended source of the CO production as observed with the neutral mass spectrometer on Giotto (9).

The affinity of POM for graphite and silicates suggests that it may be one of the constituents in the C-H-O-N dust particles found in comet Halley (10). There may also be other polymers, possibly containing atomic nitrogen or cyanide radical, that are associated with dust grains. These may be more stable at higher temperatures than POM, which dissociates under vigorous heating. If POM bonds the smallest grains through whiskerlike structures into larger grains, then this would account for the observed increase in the ratio of small particles to large particles with increasing distance from the nucleus in comet Halley (11). It could also account for the low albedo of the nucleus (12). The inactive areas of the nucleus may be covered with these particles that can trap light in the spaces between the POM whiskers. POM is also consistent with the highly porous and refractory surfacelayer material needed to insulate the ice below it from the solar radiation (13).

The idea that POM is an astrophysical material is not new. Wickramasinghe (14) suggested its existence to explain part of the interstellar extinction spectrum. Vanýsek and Wickramasinghe (15) suggested that POM can be responsible for certain observed features in the infrared spectrum of several comets. Mendis and Wickramasinghe (16) echoed these suggestions and considered additional properties of POM that strengthened the indirect evidence.

Polymer formation is one of the most characteristic properties of formaldehyde. It proceeds as an exothermic reaction. Mechanisms for polymerization at very low temperatures in interstellar space involve quantum tunneling of the activation potential (17). Cosmic radiation plays an important role in this process. However, several preliminary steps need to be investigated to complete the chemical sequence of formation, starting from the dominant constituents in interstellar clouds.

POM could have formed under the action of cosmic radiation on the surface layer of comet nuclei in the Oort cloud. However, since POM is still being released from the comet, it appears that the dust that contains POM is also deep in the interior of the nucleus. The POM must have been created in interstellar space, the presolar nebula, or the solar nebula and was then incorporated into the cometesimals at the time of their formation. This would be consistent with the hypothesis that comets are the Rosetta stone of the solar nebula (18). However, POM is not as volatile as the icy component of a comet nucleus and its affinity for dust grains would make it even more stable. Frozen water is the least volatile and most abundant component of the ices in comet nuclei, and is also relatively stable. However, most of the other volatile icy components are present only at the level of a few percent. Their primordial abundance in cometesimals may have been quite different.

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High-Resolution Electron Microscopy and Scanning Tunneling Microscopy of Native Oxides on Silicon

A. H. CARIM, M. M. DOVEK, C. F. QUATE, R. SINCLAIR, C. VORST

High-resolution transmission electron microscopy and scanning tunneling microscopy have been combined to examine the structure of the thin "native" oxide that forms on silicon surfaces at room temperature. Differences in the cleaning procedures for silicon wafers may affect the morphology of this oxide and critically influence further processing on the silicon substrates. An etch that ended with a dip in hydrofluoric acid provided a thinner oxide and a lower interface step density than did a sulfuric peroxide treatment. The availability of complementary information from high-resolution transmission electron microscopy and scanning tunneling microscopy is discussed.

HE EXPOSURE OF SILICON TO AIR AT room temperature causes a thin layer of "native" oxide to form. The properties of this oxide affect subsequent epitaxy, metallization, oxidation, and electrical behavior and thus are critical in solid-state silicon technology. Chemical and optical characteristics of the native oxide on silicon have been investigated by methods such as x-ray photoelectron spectroscopy (XPS) (1, 2), electron energy loss spectroscopy (EELS) (2, 3), and ellipsometry (1, 4, 5). Such techniques have provided information on the oxide stoichiometry, density, impurities, and growth rates. Their disadvantages are that these techniques average signals from over a large area on the sample surface

and do not directly probe the nanometerscale structure of the film.

Recently, two powerful tools have emerged for examining the structure of surfaces and interfaces. First, high-resolution transmission electron microscopy (HRTEM) has evolved into a well-characterized technique for profile imaging of interfaces (6) and surfaces (7). Second, scanning tunneling microscopy (STM) (8) provides a new method for obtaining a planar view of surface structure. In this report cross-sectional HRTEM and real-time STM imaging are combined to accurately determine native oxide thicknesses and examine silicon-oxide interface morphologies after two different cleaning procedures. Three major goals were achieved: (i) new information

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on the structure of native oxide was obtained; (ii) the ability to gather complementary information from HRTEM and STM was realized; and (iii) STM imaging of a solid-state interface through a vacuum-dielectric bilayer barrier was demonstrated.

The wafers used in this experiment were *p*-type (100) slices with a resistivity ρ between 17 and 33 Ω-cm. Two cleaning treatments were examined. The "A" cleaning involved 10 minutes of immersion in a sulfuric peroxide solution (50 ml of H₂O₂ added to an 8-liter H₂SO₄ bath just prior to wafer cleaning) at 90° to 110°C followed by 10 seconds in 1:10 HF in deionized water (DI) mixed by volume. This procedure left a nearly bare silicon surface that formed a thin native oxide layer shortly after removal from the HF (1). The "B" cleaning involved 10 minutes of immersion in a 1:3:3 solution of HNO₃-HCl-DI followed by the 10 minutes of sulfuric peroxide treatment discussed above in A. This is similar to the so-called chemical oxide treatments (9), since it is thought that a small amount of oxide forms during the final cleaning step. Three hours

A. H. Carim and R. Sinclair, Department of Materials Science and Engineering, Stanford University, Stanford, CA 94305.

M. M. Dovek and C. F. Quate, E. L. Ginzton Laboratory, Stanford University, Stanford, CA 94305. C. Vorst, Philips Research Laboratories Sunnyvale, Sig netics Corporation, 811 East Arques Avenue, Sunnyvale, CA 94088.