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MASS SPECTRA OF SPUTTERED POLYOXYMETHYLENE: IMPLICATIONS FOR COMETS[1]

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ABSTRACT

Laboratory mass spectra of sputtered polyoxymethylene, POM, reveal a mass pattern similar to that detected by the PICCA experiment on board the *Giotto* spacecraft. Both commercially available POM and radiation-synthesized POM have been used in our studies. Synthesized POM was identified by its infrared absorption spectra after proton irradiation of H_2CO condensed on silicate grains at 20 K. Laboratory results suggest that a similar type of sputtering is a possible mechanism for removing species from cometary grains.

Subject heading: comets

A repeating mass spectral pattern with broad peaks centered at 45, 61, 75, 91, and 105 amu was detected in the inner coma ($r > 4700$ km, effective mass resolution 3 amu) of comet Halley by the *Giotto*/PICCA (Positive Ion Cluster Composition Analyzer) instrument (Mitchell *et al.* 1986, 1987). Huebner, Boice, and Sharp (1987) and Huebner (1987) suggested that this mass spectrum was similar to the expected fragmentation pattern of chain molecules such as polymerized formaldehyde, $(H_2CO)_n$, known generically as polyoxymethlene, POM. Higher resolution data were also obtained by *Giotto*/PICCA ($r < 4700$ km) from 35 to 70 amu. These data are consistent with POM but also suggest the presence of other complex molecules and/or polymers (Huebner, Boyce, and Korth 1989; Mitchell *et al.* 1989).

It is thought that if POM exists on the cometary nucleus, it may be carried out to the coma on dust grains which then release polymer fragments. An unexpectedly large population of subfemtogram dust grains were detected by both dust-impact experiments on *Giotto* (McDonnell *et al.* 1986; Kissell *et al.* 1986*a*, *b*), but the mechanism for release of material from grains such as these is still an open question. One idea is that release could result from a thermal process since the temperature of these grains is expected to rise above 320 K (the approximate mean temperature of the nucleus near 1 AU; Emerich *et al.* 1986) as they are heated by solar radiation in the coma. Equilibrium temperatures close to the melting point of POM (~407 K) are thought to be a possible upper limit for these cometary grains (Hanner 1985, 1990).

Another possible release mechanism is sputtering of grains due to bombardment by coma ions. PICCA observed a "hot" ion component background ($E/q > 2$ keV/q) in the inner coma region (between 9000 and 14,000 km) during its inbound pass along with the "cold" ion ($E/q < 2$ keV/q) spectrum interpreted as POM fragments. A burst of energetic ions was also detected by the *Giotto* ion mass spectrometer (Goldstein *et al.* 1987) beginning near the contact surface (~4700 km) on its continuing inward journey. CO^+(~500 eV) was the dominant ion detected with a flux of 3.1×10^9 cm^{-2} s^{-1} (at 3000 km) and an assumed mean velocity of 60 km s^{-1} (Eviatar *et al.* 1989). Released POM fragments may be ionized by photons, electron impact, charge exchange, or ion-molecule reactions as they move outward with the bulk gas flow forming the ions detected by PICCA and may dissociate to form molecular products such as CO, CO_2, and monomeric H_2CO. An *in situ* source of POM fragments would be consistent with the extended source of cometary CO suggested by the observations of Eberhardt *et al.* (1986) and Feldman *et al.* (1989) as well as the suggestion by Snyder, Palmer, and de Pater (1989) that a distributed source of H_2CO, in addition to that produced directly from the nucleus, was required to fit the H_2CO radio data.

The idea that POM polymers could exist in cometary and interstellar materials is not new. Wickramasinghe (1974, 1975) proposed that H_2CO condenses on interstellar silicate grains as polyoxymethylene, a process which would be expected to produce a variety of other mixed polymers. The possibility that POM exists on cometary dust or in icy grains in molecular clouds was discussed by Vanysek and Wickramasinghe (1975) and Goldanskii (1979), respectively. It is known from laboratory experiments (e.g., Goldanskii, Frank-Kamenetskii, and Barkalov 1973) that irradiation of condensed H_2CO forms polyoxymethylene at temperatures as low as 20 K. There are, however, few relevant laboratory data on cometary-type ices or grains which include studies of condensation processes, irradiation effects, and removal mechanisms for H_2CO, POM, or other organic polymeric molecules which may be present (see, e.g., Huebner, Boyce, and Korth 1989 for a discussion of possible polymeric organic molecules on comets).

The fragmentation of POM has been studied by mass spectrometry (MS) of sublimated POM and secondary ion mass spectrometry (SIMS) of POM. Sublimated polymeric forms of formaldehyde were detected when solid polyoxymethylene glycol (commercially known as paraformaldehyde) was directly inserted into a mass spectrometer (Möller and Jackson 1990; Boice, Naegeli, and Huebner 1989). Paraformaldehyde is a type of POM with water attached as an end group. As the

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temperature of the source was raised above 300 K, peaks were observed at 30(H$_2$CO)$^+$, 47[OH(H$_2$CO)]$^+$, 61[H(H$_2$CO)$_2$]$^+$, 77[OH(H$_2$CO)$_2$]$^+$, 91[H(H$_2$CO)$_3$]$^+$, 107[OH(H$_2$CO)$_3$]$^+$, and 121[H(H$_2$CO)$_4$]$^+$ amu. These experiments show that polymeric forms can sublime from the pure solid. The same polymeric forms were also detected from water solutions containing POM.

SIMS of POM at 300 K has recently been reported by Mahaffy (1990). Fragments of POM resulted from desorption of positive ions after impact by 1–4 keV cesium ions. The most intense peaks were observed at 30, 44, 60, (72, 74), (89, 91), (103, 105), (119, 121), and 133 amu. The peaks observed at 30, 44, and 60 amu correspond to (H$_2$CO)$^+$, CO$_2^+$, and (H$_2$CO)$_2^+$, respectively. The higher mass of the two peaks in each group is assigned to 74[CH$_2$(H$_2$CO)$_2$]$^+$, 91[H(H$_2$CO)$_3$]$^+$, 105[CH$_3$(H$_2$CO)$_3$]$^+$, and 121[H(H$_2$CO)$_4$]$^+$.

In this *Letter* we discuss the mass spectrum of fragments sputtered from POM by protons. The fragmentation pattern detected results from sputtering with light energetic projectile ions in contrast to heavy low-energy Cs$^+$. We also sputtered radiation-synthesized POM formed on silicate grains after condensation and irradiation of monomeric formaldehyde.

We have sputtered paraformaldehyde (purified; Fisher Scientific Co.) in a vacuum system at 300 K using 700 keV protons (proton beam current was $\sim 1.5 \times 10^{-7}$ A corresponding to 9×10^{11} protons s^{-1}). Sputtered fragments were detected with a Dycor (Model M200M) quadrupole mass spectrometer (see Moore, Donn, and Hudson 1988 for a discussion of the experimental set-up). The resulting laboratory mass spectrum shown in Figure 1 (curve B) from 40 amu to 160 amu spans more than three decades in intensity and has a repeating pattern similar to the PICCA data (curve A). Since peaks were not detected when the mass spectrometer's ionizer voltage was turned off, the dominant species produced during irradiation were neutral fragments. Laboratory measurements of the yield, Y (number of sputtered molecules per incident ion), are planned for future experiments. A lower limit estimate would be $Y = \sim 0.2$ ($T < 80$ K), based on the approximation that Y is inversely proportional to the heat of sublimation, H_s, of the target. Since H_s POM $\cong 1.5 \times H_s$ H$_2$O, and $Y \cong 0.3$ for 700 keV protons on water ice (Johnson *et al.* 1989), then $Y \cong 0.2$ for 700 keV protons bombarding POM (1 keV protons, more typical of solar wind energies, would have approximately twice the yield). This is a lower limit estimate because it is known that at $T > 100$ K, Y(H$_2$O) is temperature-dependent and increases by nearly a factor of 5 by 150 K (1/2 melting point) (Brown *et al.* 1980). Y(POM) at 300 K ($\sim$3/4 melting point) would be temperature-dependent, but these sputter-enhanced vaporization yields have not been measured.

In Figure 1, the most intense signals are at 28, 29, 30, and 44[4] amu which are attributed to CO$^+$, HCO$^+$, H$_2$CO$^+$ and CO$_2^+$. This result suggests that if the extended source of CO and H$_2$CO is from the dissociation of (H$_2$CO)$_n$, then HCO and CO$_2$ species may also be present. The next strongest peaks were observed at (60, 61), (73, 75), (89, 91), 105, (119, 121), (131, 135) amu. As shown in Table 1, the higher mass of the two peaks in each group can be assigned to (H$_2$CO)$_n$ ions with either an attached CH$_3$ group or H atom. The actual structure of the fragments was not determined. These assignments refer only to the masses of each ion and were confirmed with mass spectra we obtained after sputtering deuterated paraformaldehyde, (D$_2$CO)$_n$ (99.8 atom %D, MSD isotopes). It is interesting and somewhat surprising that the mass pattern observed from SIMS of POM is so similar to the mass pattern from proton sputtering followed by electron ionization inside the mass spectrometer.

An estimate of the broadening experienced by ions detected by PICCA was used to similarly broaden several of the most

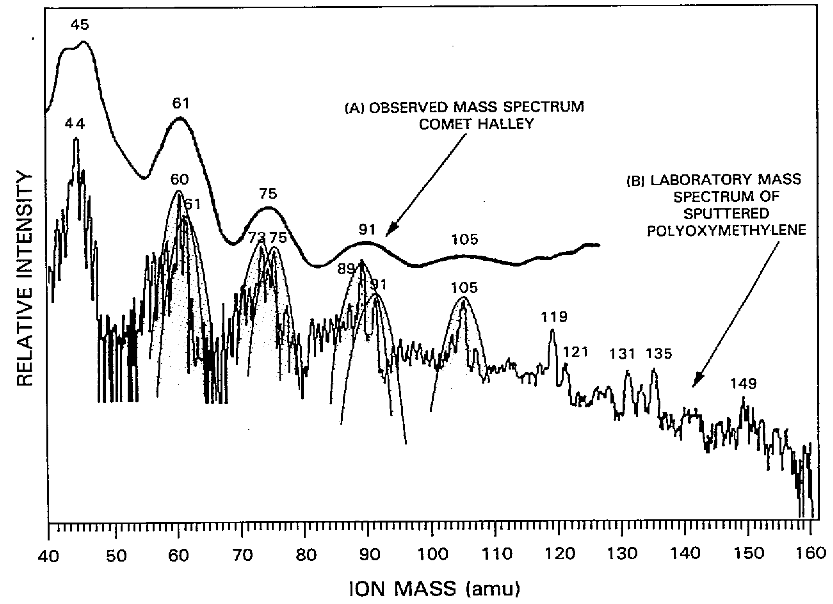

FIG. 1.—The upper curve reproduces the mass spectrum measured by the PICCA instrument on board the *Giotto* spacecraft in the inner coma of comet Halley. This is compared with the laboratory mass spectrum of fragments produced during sputtering of polyoxymethylene at 300 K with 700 keV protons. The shaded areas over several of the peaks in the laboratory data are estimates of the degree of broadening experienced by similar ions detected by PICCA.

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[4] The correct assignment of the most intense peak in this group is 44 amu (CO$_2^+$), not 45 amu (Moore and Tanabé 1989, 1990). Mass 45 (H$_2$CO)CH$_3^+$ is present but less intense.

TABLE 1

TENTATIVE ASSIGNMENT OF POM FRAGMENTATION PEAKS

m/e	Ion$^+$	*m/e*	Ion$^+$
61.........	$(H_2CO)_2H$	60.........	$(H_2CO)_2$
75.........	$(H_2CO)_2CH_3$	73.........	$(H_2CO)_2CH$
91.........	$(H_2CO)_3H$	89.........	$(H_2CO)_2HCO$
105.........	$(H_2CO)_3CH_3$	...	
121.........	$(H_2CO)_4H$	119.........	$(H_2CO)_3HCO$
135.........	$(H_2CO)_4CH_3$	131.........	$CO(H_2CO)_3CH$
		133.........	$(H_2CO)_4CH$

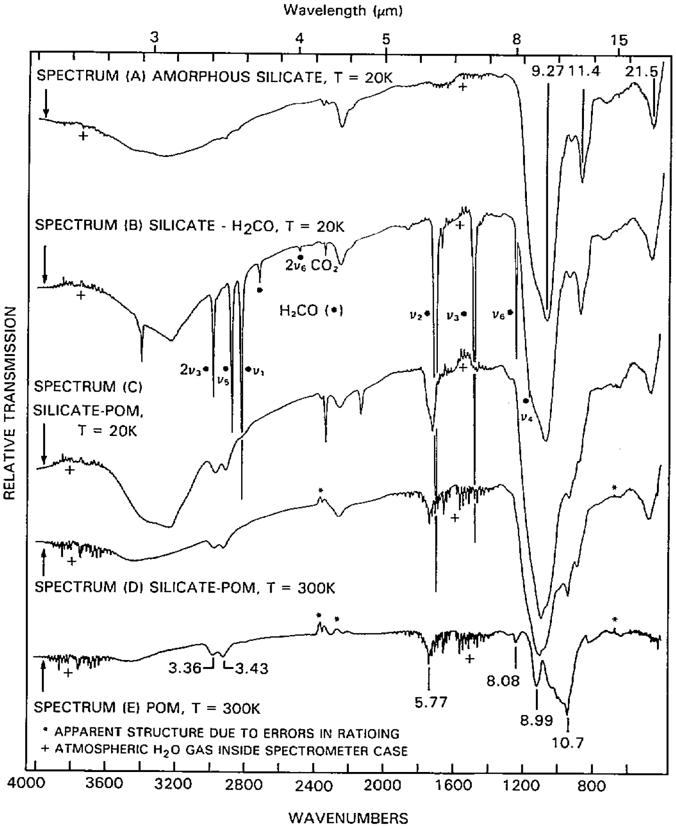

FIG. 2.—Infrared spectra recorded at various stages of the experiment are stacked for comparison. Spectrum A: Amorphous silicate grains at 20 K. The SiO stretch band is near 10 μm. Spectrum B: Formaldehyde gas is condensed on the silicate grains forming a silicate-H_2CO composite at 20 K. Spectrum C: A silicate-POM sample at 20 K results from the proton irradiation of the silicate-H_2CO composite. Spectrum D: Silicate-POM sample at 300 K. This sample was sputtered with protons. Spectrum E: The ratio spectrum (silicate-POM/silicate) reveals the dominant features of the synthesized POM.

intense peaks detected in our laboratory data. The shaded Gaussian-shaped envelopes in Figure 1 (curve B) represent an estimate of this broadening. It appears that much of the "width" of the PICCA data can be fitted with POM fragmentation (although the PICCA spectrum still shows greater width). The intensity of the peaks decreases with incrasing mass as does the PICCA data, although the spacecraft data decrease more rapidly.

In a separate experiment, POM was synthesized on silicate grains and then sputtered to see if any differences in the fragmentation pattern could be measured. Infrared transmission spectra were used to identify the different stages leading to POM formation on amorphous silicate grains (SiO_x) in the laboratory. These grains were prepared in a flow condensation apparatus (Nuth *et al.* 1988). Gas mixtures of hydrogen, silane, and oxygen (10:1:1 by volume) were introduced into the flow system's furnace tube whose temperature was near 870 K. SiO_x was condensed onto polished substrates especially designed for infrared spectroscopy and irradiation. The characteristics of these silicates will be discussed elsewhere. Figure 2 (spectrum A) shows the infrared spectrum of these grains from 2.5 to 25 μm. The dominant SiO stretching vibration feature occurs near 10 μm. H_2CO gas was condensed onto the silicate at 20 K; see spectrum B. Proton irradiation was used to polymerize H_2CO monomers and form a silicate-POM composite at 20 K (spectrum C). Spectrum D is that of the silicate-POM warmed slowly to 300 K. This sample was subsequently sputtered. Spectrum E is the ratio spectrum of silicate-POM/silicate revealing the features of POM, the strongest of which are near 10 μm. When this silicate-POM sample was bombarded with 700 keV protons, the same fragment pattern was detected at approximately the same intensity as shown in Figure 1 (curve B) for the commercial paraformaldehyde sample.

It is difficult with this preliminary data to estimate the importance of the sputtering mechanism in the coma of comet Halley with any certainty. If we assume that CO^+ is a dominant sputtering ion and that POM fragments are sputtered from grains inside the contact surface, we can approximate a lower limit yield estimate of $Y \sim 4$ POM fragments per CO^+ ion-collision which is $\frac{1}{3}$ the yield during bombardment of water ice by C^+($\sim$20 eV amu^{-1}) (there are no experimental data for sputtering with CO^+). By combining the largest effective cross sectional area of grains calculated at 2000 km, 10^{-12} cm^2 cm^{-3} (McDonnell *et al.* 1987), with the measured CO^+ flux, we estimate a probability > 50% of at most two sputtering events per 1000 cm^3 or eight POM fragments per 1000 cm^3. This predicted sputtering is the order of $\sim 10^3$ too small to account for the estimated 3–30 H_2CO^+ cm^{-3} (sum of all ions mass 60–121 amu) near 10,000–5000 km (Mitchell *et al.* 1987).

Further studies of experimental yields of sputtered molecules from POM due to incident ions with energies below a few keV amu^{-1} are required before the importance of the role of POM sputtering in cometary comae can be more accurately estimated. It is not known if the sputtering enhanced vaporization yield could increase by as much as a factor of 10^3 with increased temperature or if the yield is enhanced when sputtering from small grains compared to sputtering from a thin film. Further experiments are required to determine the mass distribution of neutral sputtered fragments and the distribution due to ionization. Since it is likely that there exists in comets a variety of complex nonvolatile organic residues, which could contribute to the width of the PICCA data, we have begun an investigation of the sputtered fragments from different organic residues.

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