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Studies of Proton-Irradiated Cometary-Type Ice Mixtures

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Radiation synthesis has been proposed as a mechanism for changing the nature of the outer few meters of ice in a comet stored 4.6 billion years in the Oort cloud and may explain some of the differences observed between new and more evolved comets. Cometary-type ice mixtures were studied in a laboratory experiment designed to approximately simulate the expected temperature, pressure, and radiation environment of the interstellar Oort cloud region. The 2.5- to 15-μm infrared absorption features of thin ice films were analyzed near 20°K before and after 1 MeV proton irradiation. Various ice mixtures included the molecules H_2O, NH_3, CH_4, N_2, C_3H_8, CO, and CO_2. All experiments confirm the synthesis of new molecular species in solid phase mixtures at 20°K. The synthesized molecules, identified by their infrared signatures, are C_2H_6, CO_2, CO, N_2O, NO, and CH_4 (weak). Synthesized molecules, identified by gas chromatographic (GC) analysis of the volatile fraction of the warmed irradiated ice mixture, are C_2H_4 or C_2H_6, and C_3H_8. When CH_4 is present in the irradiated ice mixture, long-chained volatile hydrocarbons and CO_2 are synthesized along with high-molecular-weight carbon compounds present in the room temperature residue. Irradiated mixtures containing CO and H_2O synthesize CO_2 and those with CO_2 and H_2O synthesize CO. Due to radiation synthesis, ~1% of the ice was converted into a nonvolatile residue containing complicated carbon compounds not present in blank samples. These results suggest that irrespective of the composition of newly accreted comets, initial molecular abundances can be altered and new species created as a result of radiation synthesis. Irradiated mixtures exhibited thermoluminescence and pressure enhancements during warming; these phenomena suggest irradiation synthesis of reactive species. Outbursts in new comets resulting from similar radiation induced exothermic activity would be expected to occur beginning at distances of the order of 100 AU.

I. INTRODUCTION

Cometary Theory and Observations

It is a widely accepted postulate that comets were formed simultaneously with the solar system (Delsemme, 1977; Donn and Rahe, 1982) and have been stored for 4.6 billion years in the Oort cloud region. Cometary nuclei in this interstellar environment experience an ionizing particle flux due to cosmic rays and an ultraviolet photon flux. Ultraviolet photons penetrate material to ~10^{-5} cm and affect only the cometary surface. Cosmic rays however have considerable penetrating power as shown in Table I for protons in water ice.

The exposure of comets to the environment of interstellar ionizing radiation may result in significant chemical and physical changes in the outermost irradiated ice (Shul'man, 1972; Donn, 1976; Whipple, 1977). The subsequent reprocessing may significantly alter the original properties of the ice and account for some of the differences observed between new and more evolved comets. The purpose of this research was to experimentally study the effects of 1-MeV proton radiation on ice mixtures expected to occur in comets. The 1-MeV protons simulate the chemically effective low energy range of cosmic rays and are also experimentally convenient.

Observations support the hypothesis that water is the dominant volatile in most comets (e.g., Jenkins and Wingert, 1972; Keller

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TABLE I

RANGE OF PROTONS IN WATER ICE[a]

Proton energy (MeV)	Range (cm)
0.5	9.1×10^{-4}[b]
1.0	2.1×10^{-3}[b]
5.0	3.5×10^{-2}[b]
10.0	1.1×10^{-1}[c]
100.0	7.6[c]

[a] The range of protons in water ice is equal to the range of protons in liquid water since we have adopted the same mass density (ρ) for both phases. The integrated loss of energy of the penetrating proton, which determines the proton range, is proportional to the mean density of electrons (N_e) in the target (e.g., Anderson and Zeigler, 1977). Since $N_e \sim \rho$, the range of a proton can be calculated if different densities occur due to phase changes or ice compactions.

[b] Northcliffe and Shilling (1970).

[c] Barkas and Berger (1964).

and Thomas, 1975; Jackson *et al.*, 1976; Weaver *et al.*, 1981). In some comets, carbon dioxide or carbon monoxide may also be a major volatile (Delsemme, 1977; Feldman *et al.*, 1974; A'Hearn *et al.*, 1977; Delsemme and Combi, 1979), whereas ammonia and methane are examples of molecules suggested as minor constituents in the cometary ice.

In most respects, the observed features of new and more evolved comets are very similar. There are, however, some cometary observations which support the idea that new comets have a more volatile icy surface layer than evolved comets. One type of observational data is based on the measured rate of variation of cometary brightness for comets of different ages. Whipple (1978) showed that a typical new comet brightens rapidly and becomes visible at great solar distances and then more slowly near perihelion ($n \simeq 2.4$, where the observed cometary brightness is $\sim r^{-n}$, the comet–sun distance is r, and the value of n is derived for each comet by curve fitting). The behavior of new comets at great solar distances supports one of the conclusions of Oort and Schmidt (1950) that these comets contain more volatile gases. After perihelion, new comets show statistically the same luminosity decrease as older comets ($\bar{n} \simeq 3.4$). Whipple (1978) suggested that this could arise from the buildup of meteoritic material. A buildup of a chemical insulating layer may also occur. These observations imply that the supply of more volatile ice has been exhausted before the first perihelion is reached. Marsden and Sekanina (1973), based on the statistics of cometary orbits, concluded that observed comets with $q > 3$ AU (where $q \equiv$ perihelion distance) are mostly new comets. Since there is no a priori reason for that statistical distribution, a possible explanation is that after their first apparition comets are much fainter than they were initially and are not as readily detectable at these distances.

The possible existence of super-volatile ices on the surface of new comets is supported also by the observations of tails in new distant comets. Observations analyzed by Sekanina (1973) showed that each of two new comets exhibited a particle tail which he estimated had been released at distances as large as 15 AU. His calculations showed that a substance more volatile than water snow, and probably comparable to or even more volatile than methane, was required to supply the necessary momentum to lift the grains into the tail. Cometary activity at very large heliocentric distances is also envisioned by Sekanina (1982) to explain the dust observed around the relatively inactive new comet, Bowell (1980b).

What is definite is that "new" comets show enhanced activity at large heliocentric distances. The cause of this behavior, as just discussed, is generally interpreted to be super-volatile ices in the outer shell of the nucleus. Although the differences among individual comets are large, Whipple (1977) adopted, as a working model, a layered cometary nucleus. For a new comet, this structure includes an outer layer formed of very volatile material extending to depths of a few hundred grams per square centimeter. Whipple speculated that this frosting could result from cosmic ray irradiation of the ice during the 4.6-billion year storage time in the Oort cloud. Radiation-synthesized radicals would be concentrated in this outermost layer. These radicals would react exothermically with moderate solar heating at solar distances $r > 3$ AU resulting in the vaporization of the frosting. An outflow of solid particles would be produced. If this frosting is removed during the first perihelion passage, the brightness of the comet could decrease by several magnitudes during the next apparition. This model could explain the large "disappearance rate" of newer comets with perihelion distance $q > 3$ AU.

An apparently opposite speculation by Donn (1976) was that intense radiation synthesis would tend to polymerize the simple, volatile ices resulting in a darker, less volatile outer zone with a lower albedo compared to the inner protected ices. He suggested that this less volatile outer zone was in contradiction with the greater activity of new comets. However, this may not be the case. This layer may not be completely converted to inert polymer resulting in a mixed-polymer reactive ice shell close to the surface. This heavily irradiated outer layer will be darker and absorb a larger fraction of sunlight than the original icy material. The additional heating would make this shell significantly more active than the original material that is exposed in almost-new comets. Thus, Whipple's or Donn's prediction leads to more active new comets.

Cosmic Ray Environment

The interstellar particle radiation environment is modeled as a cosmic ray flux which, according to cosmochemical evidence, has been roughly constant throughout the age of the solar system (Meyer *et al.*, 1974). Although the flux and spectrum of interstellar cosmic rays cannot be directly measured, it is estimated that 93% of the particle flux is due to protons, 6% helium nuclei, and 1% heavier weight nuclei (Meyer *et al.*, 1974). The interstellar electron cosmic ray flux is 1/10 to 1/100 the proton flux for energies below 100 MeV (Goldstein *et al.*, 1970). An estimate of the total galactic cosmic ray intensity is 8×10^2 MeV $\mathrm{cm}^{-2}\ \mathrm{sec}^{-1}\ \mathrm{ster}^{-1}$; the mean energy of a cosmic ray proton is 2×10^3 MeV (Shul'man, 1972). A cometary surface exposed to this radiation for 4.5 billion years would undergo 3.5×10^{17} impacts/cm^2.

The energy density deposited in a cometary icy nucleus over 4.5 billion years has been estimated by Donn (1976), and independently by Whipple (1977). For energies greater than 100 MeV, the extrapolated interstellar cosmic ray proton differential energy spectrum is assumed to be a power law of the form $dN/dE \sim E^{-\gamma}$, where $\gamma \simeq 2.5$ (Goldstein *et al.*, 1970). Donn (1976) used this energy spectrum and assumed that the distribution was valid to energies as low as 10 MeV. These data were combined with the stopping power of water ice to estimate the accumulated energy deposited in an icy cometary nucleus as a function of depth. The calculated results indicate that sufficient energy is accumulated in the top layers of a cometary nucleus for significant radiation synthesis to occur. The top 10 cm of the cometary ice effectively stops protons with energies below 120 MeV. Protons with greater energy penetrate to deeper ice layers. Because the number of cosmic ray protons is decreasing as $E^{-2.5}$ the concentration of reacted molecules diminishes in a corresponding manner. Table II compares the percentage of reacted molecules predicted by Donn (1976) and Whipple (1977).

Three previous experiments have been carried out on the effects of particle radiation on ice mixtures at low temperature: (1) Berger (1961) irradiated a mixture of water, ammonia, and methane at 77°K with 12 MeV protons to a total incident fluence of 1.24×10^{14} protons cm^{-2} (calculated from Berger assuming the incident flux given as 0.5 μA/sec was to read 0.5 μA/cm^2). He estimated that the number of proton im-

TABLE II

ESTIMATED ENERGY ACCUMULATED IN COMETARY NUCLEI IN 4.5 BILLION YEARS

Absorbed fluence in top 20 cm ice layer	Approximate % of molecules reacted[a] in 20-cm layer located at:		
	Surface	Depth of 1 m	Depth of 2 m
Donn (1976)			
3.49×10^{19} MeV cm^{-2}	50	16	10
Whipple (1977)			
2.4×10^{19} MeV cm^{-2}	34	30	17

Note. Oort cloud dose ≡ 41 eV/molecule. An "Oort cloud dose" is defined as the eV/molecule estimated to be deposited in the top 20-cm layer of a cometary ice stored for 4.5 billion years in the Oort cloud region. Using the average absorbed fluence predicted by Donn (1976) and Whipple (1977), 2.9×10^{19} MeV/cm^2, results in an Oort cloud dose = 41 eV/molecule (the average molecular weight adopted was 17 g/mol).

[a] The amount of absorbed energy required to create a new product is typically 100 eV/molecule (e.g., Davis and Libby, 1964).

pacts cm^{-2} during the experiment approached the order of magnitude of those sustained by a comet the age of the solar system (actually, 10^{17} proton impacts cm^{-2} is calculated based on data discussed by Shul'man, 1972 or Donn, 1976). Analysis of the volatile and nonvolatile fractions after irradiation showed the presence of acetone, the suggestion of purine or pyrimidine compounds, and urea. (2) Oro (1963) irradiated a mixture of water, ammonia, and methane at 77°K with 5-MeV electrons and measured a 4.6% conversion of labeled [^{14}C]methane from a volatile to a nonvolatile form. Analysis of the nonvolatile residue suggested the presence of purines and pyrimidines. (3) Pirronello *et al.* (1982) irradiated an ice mixture of equal parts of isotopically labeled water and carbon dioxide at ~9°K with 1.5-MeV helium ions (10^{13}–10^{14} incident ions over a 4-cm^2 sample) and observed the synthesis of formaldehyde, H_2CO. The production rate of H_2CO was ~3.7 molecules per incident ion for ice ~1000 monolayers thick. The formaldehyde was detected using a mass spectrometer which analyzed the volatiles released by sublimation from the irradiated ice during warming. Experiments investigating the effects of radiation in pure ices have been carried out by various investigators. These investigations include γ-irradiated CH_4, H_2O, and NH_3, and e-irradiated C_2H_2 and D_2O (Davis and Libby, 1964; Matheson and Smaller, 1955; Floyd *et al.*, 1973; Glasel, 1962, respectively). All of these experiments suggest that interesting low-temperature chemistry can occur as the result of particle radiation synthesis.

An extensive program at Leiden has contributed significant results on the effects of ultraviolet photolysis on low-temperature ice mixtures (e.g., Greenberg, 1982; Hagan *et al.*, 1979). These mixtures (e.g., $CO + H_2O + NH_3 + CO_2$) are simulations of ice mantles on interstellar grains. Their results show: (1) the synthesis of new products at 10°K, (2) luminescence and pressure enhancements during warming, and (3) a room-temperature residue. The comparison between ultraviolet and particle irradiated ices is a complex task and one that is not addressed in this paper. In general, it is expected that at the molecular level, all kinds of ionizing radiation have qualitatively the same effect (e.g., Dertinger and Jung, 1980).

Recent work has shown that charged particles effectively erode frozen volatiles (Brown *et al.*, 1980a,b). The number of molecules sputtered in a 7–10°K ice per incident 1.5-MeV He ion is: CH_4, 120, CO_2, 120, NH_3, 140, SO_2, 32, H_2O, 8 (Johnson *et al.*, 1982). These studies are used to predict the effects of competition between collection and loss of volatiles on icy bodies and the nature of the surface composition. Implications for comets are also discussed by Johnson *et al.* (1982).

II. EXPERIMENTS

In previous experiments the effects of particle radiation on low-temperature ices were deduced by analyzing the volatiles which sublimed during warming or by analyzing the residue after warming to room temperature. The present research on proton-irradiated cometary-type ice mixtures measured the infrared absorption spectrum of the ice at 20°K, before, during, and after irradiation. The ice characteristics during warming and the residue after warming to room temperature were also investigated. Mixtures include some combination of the following molecules: H_2O, NH_3, CH_4, N_2, C_3H_8, CO, and CO_2. These combinations approximately simulate the abundant elemental composition of comets. The extent of chemical changes is not expected to be sensitive to the molecular composition; the specific product will depend on composition. More experimental details are given elsewhere (Moore, 1981). The sputtering of ice films, the expected difference between thin films and bulk ice samples, and the emission of secondary electrons from the aluminum sample substrate are discussed by Moore. In general, these effects are small and therefore assumed to have negligible influence on these experiments.

The source of protons used in this experiment was a High Voltage Corporation 2.5-MeV Van de Graaff accelerator at the NASA/GSFC. The proton energy was 1 MeV, and the beam current was of order 10^{-7} A (1.25×10^{11} protons cm^{-2} sec^{-1} over the 5-cm^2 sample area). This flux incident on a 1-μm-thick ice film for 4 hr results in an absorbed fluence equivalent to that predicted for the top 20-cm layer of a comet exposed for about 1.5 billion years in the Oort cloud. The absorbed fluence (MeV cm^{-2}) in an ice film was calculated from: incident flux × irradiation time × (stopping power × ice density)[2] × ice thickness. To prevent contamination of the film from the accelerator vacuum chamber, a 3.1×10^{-5}-cm-thick nickel foil (0.64-cm diameter) was placed in the beam tube and was used to isolate the Van de Graaff vacuum from the ice sample vacuum area. Approximately 3% of each proton's energy was lost as the result of passage through the nickel foil.

Figure 1 is a schematic of the experimental arrangement and shows the low-temperature closed-cycle cryostat attached to an ion-pumped vacuum system and the Van de Graaff accelerator. Figure 2 is a cut-away drawing of the sample area of the cryostat. Ice films were formed by condensing a gas mixture on the aluminum substrate whose minimum temperature was near 20°K, several degrees above the lowest temperature of the cryostat's cold end due to thermal resistance. The substrate could be maintained at any temperature between 20 and 300°K with a temperature stability of ±1.0°K. One surface of the aluminum substrate was polished to a high reflectivity. The opposite side was anodized with sapphire. This anodizing provided a low thermal resistivity along with a high electrical resistivity (required for the measurement of the proton beam current). After deposition, the ice sample was irradiated with 1-MeV protons.

[2] The electronic stopping power for 1-MeV protons is 308 MeV cm^2 g^{-1} (Northcliffe and Shilling, 1970). The density of water ice was assumed to be 1 g cm^{-3}. A 1-μm-thick ice film absorbs approximately 3% of the energy of each 1-MeV proton. Our calculations can be rescaled for a different ice density.

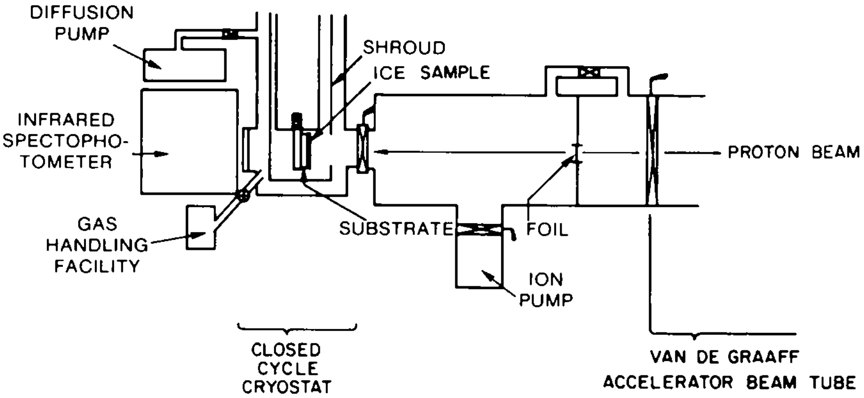

FIG. 1. Arrangement of spectrophotometer, low-temperature cryostat, and Van de Graaff generator. Ice sample is shown facing in the direction of the proton beam. If rotated 180°, the infrared spectrum of the ice sample can be measured.

The infrared spectrum of the ice could be measured before, during, and after irradiation by rotating the ice sample. A Perkin–Elmer 621 double-beam spectrophotometer was used to measure the absorption spectrum of the deposited ice between 2.5 and 15 μm. The sample beam from the spectrometer was directed onto the deposited ice film. This beam passed through the ice, reflected from the aluminum mirror substrate, and then passed a second time through the ice before it was recombined with the reference beam of the spectrometer. By using the measured infrared spec-

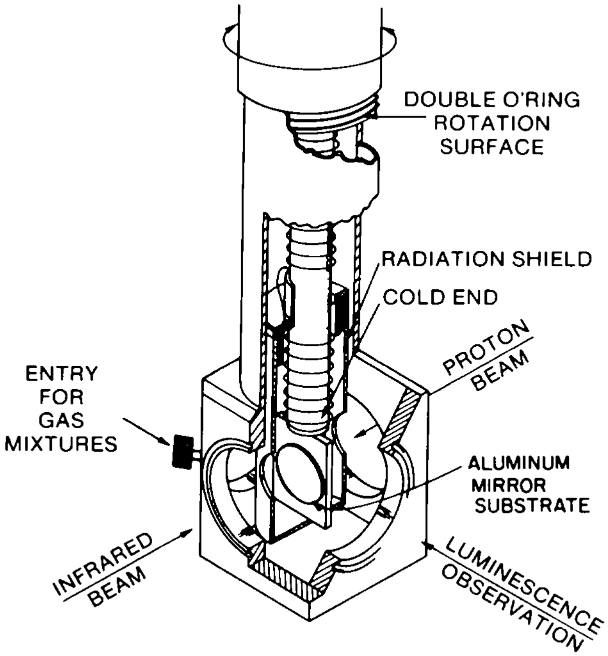

FIG. 2. The sample area of the cryostat. Ice samples are formed on the cooled aluminum mirror substrate by condensation of premixed gases.

trum of the ice, the equivalent film thickness of each molecular constituent in the ice was calculated using the standard Lambert–Bouguer radiation law and known absorption coefficients. The total thickness of a deposited ice mixture was assumed to be the sum of the thicknesses of each molecular component.

The analysis of the spectrum of irradiated ice mixtures from 2.5 to 15 μm involved the identification of new absorption features in the infrared spectrum of the original ice. In an original mixture containing $H_2O + NH_3 + CH_4$ (see Fig. 3, Before), the ν_1 and ν_3 bands of ammonia and the ν_1 band of water combine to form a large absorption band centered near 3300 cm^{-1}. The ν_3 fundamental of methane forms a sharp line centered at 3110 cm^{-1}. Near 1600 cm^{-1}, the ν_4 fundamental of ammonia and the ν_2 fundamental of water combine to form a small band. At 1300 cm^{-1} is the ν_4 fundamental of methane, at 1090 cm^{-1} the ν_2 fundamental of ammonia, and at ~800 cm^{-1} the libration band of water. When CO_2 was substituted as a source of carbon, its ν_3 fundamental was observed at 2342 cm^{-1}, and ν_2 at 654 cm^{-1} and 660 cm^{-1} (unresolved); CO as a source of carbon gives a sharp absorption fundamental at 2124 cm^{-1}; and when substituting N_2 for NH_3 as a source of nitrogen there are no absorptions in the 2.5- to 15-μm region. Gaseous carbon dioxide and water vapor, present in the spectrophotometer, were difficult to completely remove through purging. The narrow absorptions typical of these gases are superimposed on the spectra of all ice mixtures and are especially noticeable around 2.5–4, 4.2, and 5–7.5 μm. All spectra have been drawn from the original data but no attempt was made to exactly reproduce the line positions of these gas absorptions. These atmospheric lines have been completely removed from the 100% lines (Figs. 3–5) for convenience. Identification of synthesized species was based on numerous reference spectra of 20°K deposits of $H_2O + NH_3 + CH_4$ ices containing a fourth molecule (less than 10% by volume). The selection of the fourth molecule was based on its expected synthesis.

Several blank samples were studied under experimental conditions identical to those using ice mixtures. These blank samples monitored the possible contribution of contaminants. A typical blank spectrum showed that the gases H_2O and CO_2 were cryopumped in small amounts onto the low-temperature substrate. These molecules originated from the unbaked walls of the vacuum system. No other molecular contaminants were observed.

When irradiated ice samples were warmed, the volatile fraction could be collected and analyzed using (e.g.) gas chromatographic techniques. The detection of thermoluminescence from other irradiated samples during warming was made using a 1P21 cooled photomultiplier. Concurrent pressure enhancements in the vacuum system were recorded by monitoring the ion pump current which is directly proportional to the pressure.

A summary of the experiments included in this paper is given in Table III. Experiments are divided into six sets determined by the composition of the initial ice mixture. Comments are included to help direct the reader to the corresponding figure or table in the discussion.

III. RESULTS

Low Temperature

Experiment set I was a study of irradiated $H_2O + NH_3 + CH_4$ ice mixtures at 20°K using 1-MeV protons. Ice mixtures within this and within other "sets" showed generally similar results after irradiation. Figure 3 shows the infrared spectrum of an $H_2O + NH_3 + CH_4$ ice (set Ia) before and after irradiation. A list of the new absorption lines observed after irradiation is given in Table IV. In addition to the synthesis of ethane (C_2H_6), CO_2, and CO, the 2040-cm^{-1} line is suggestive of an N–N–N bonded molecule. The synthesis of CO_2 was con-

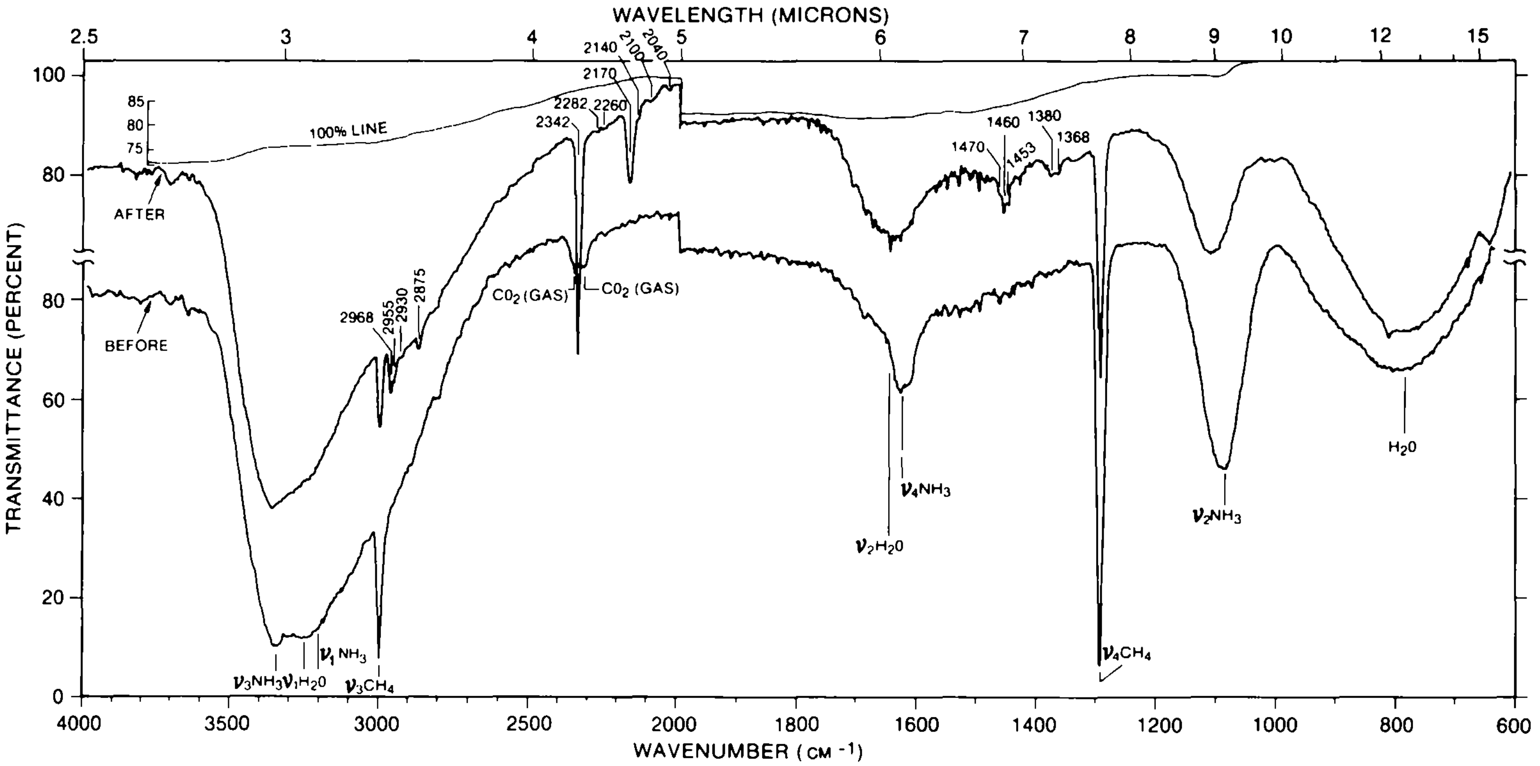

FIG. 3. Infrared spectrum of an $H_2O + NH_3 + CH_4$ (~1 : 3 : 2) ice mixture at 20°K before and after irradiation with 1-MeV protons. The estimated absorbed fluence was 2×10^{14} MeV/cm^2 in the ~2.7-μm-thick film. CH_4 is noticeably decreased after irradiation. The positions of synthesized species are marked. The absorption line at 2342 cm^{-1} results from synthesized CO_2.

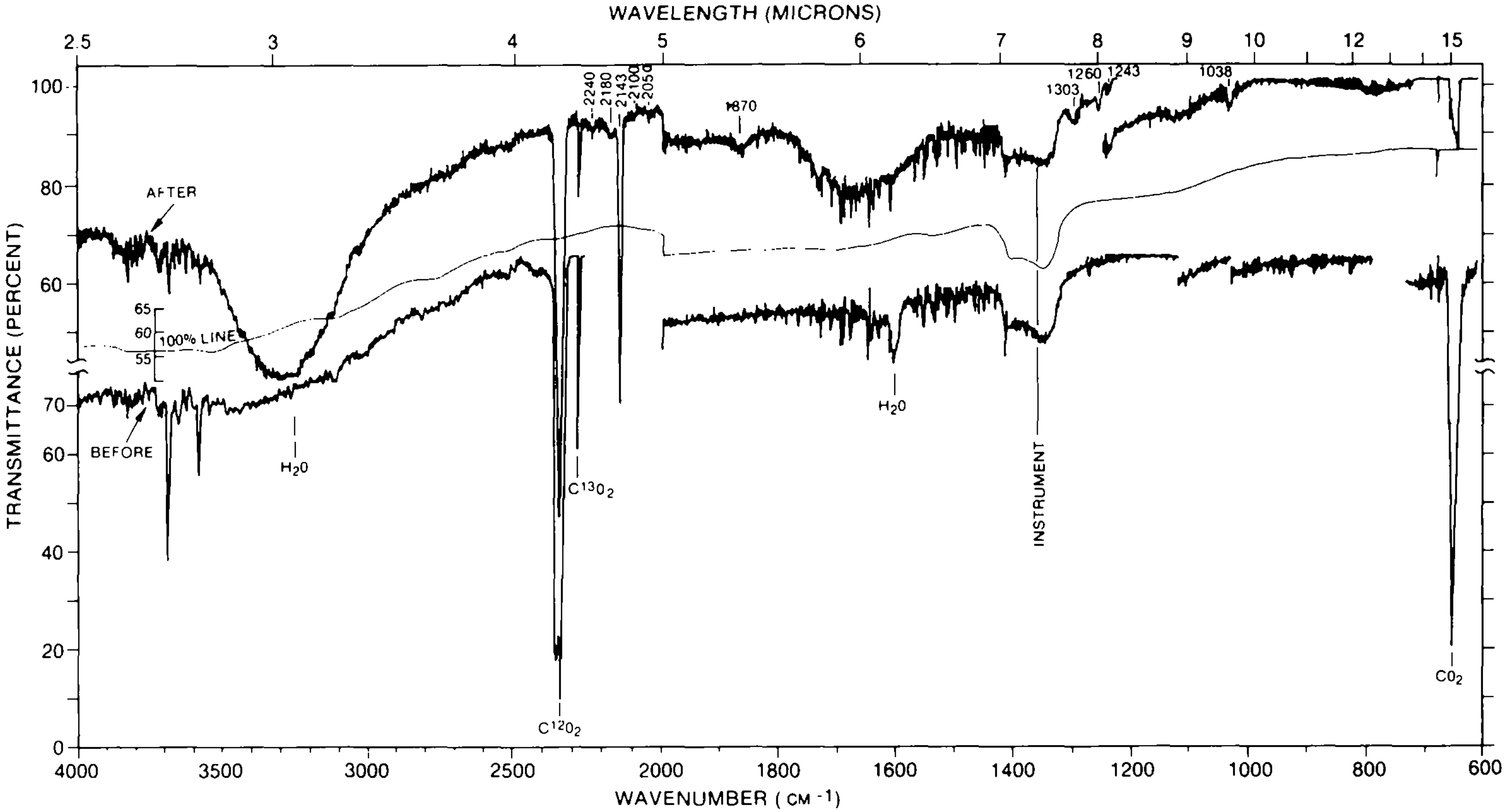

Fig. 4. Infrared spectrum of an $H_2O + N_2 + CO_2$ (~1 : 1 : 1) ice mixture at 20°K before and after irradiation with 1-MeV protons. The estimated absorbed fluence was 5×10^{12} MeV/cm^2 in the ~0.1-μm-thick film. After irradiation CO_2 is noticeably decreased. The absorption line at 2143 cm^{-1} results from synthesis of CO.

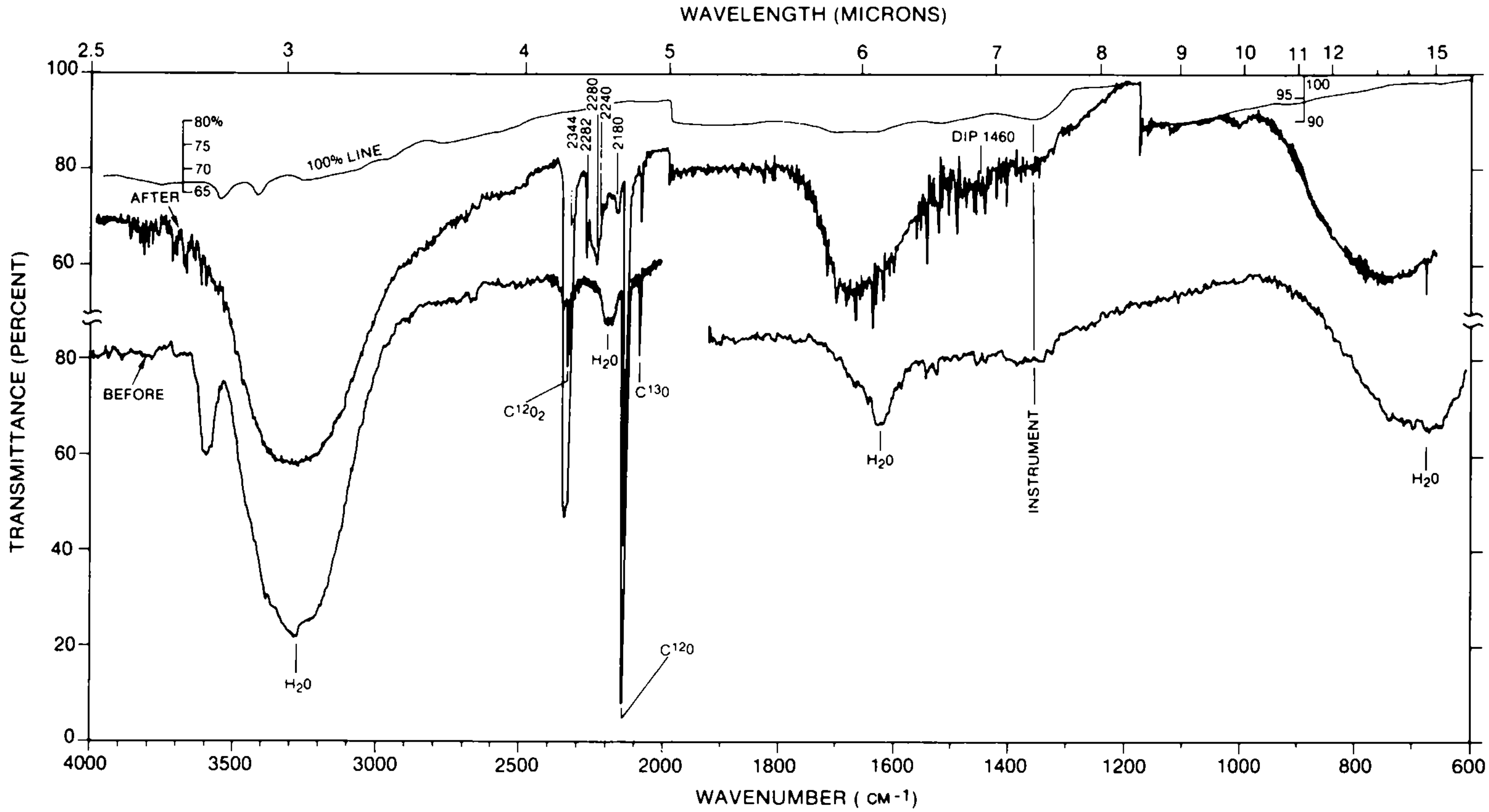

FIG. 5. Infrared spectrum of an $H_2O + N_2 + CO$ (~5 : 1 : 1) ice mixture at 20°K before and after irradiation with 1-MeV protons. The estimated absorbed fluence was 5×10^{13} MeV/cm^2 in the film which was estimated to be <1-μm-thick. After irradiation, CO is noticeably decreased. The increase in the absorption line at 2344 cm^{-1} results from the synthesis of CO_2.

TABLE III

EXPERIMENTS

Experiment set	Ice mixture	Approximate mass ratio[a]	Thickness (μm)	Irradiation time (hr)	Absorbed fluence (MeV cm^{-2})	Incident flux (E_{H^+} = 1 MeV) (MeV cm^{-2} sec^{-1})	Comments
Ia	$H_2O + NH_3 + CH_4$	(2:5:4)	2.7	6.3	1×10^{14}	2.0×10^{11} (max)	Spectrum: Fig. 3, Table IV
b		(2:7:4)	2.6	0.6	6×10^{12}	3.5×10^{10}	
c		(1:10:7)	2.2	2.0	2×10^{13}	5.1×10^{10}	
d		(1:3:2)	2.3	2.8	4×10^{13}	5.5×10^{10}	Residue: Fig. 7
e		(1:4:2)	1.5	2.0	2×10^{13}	5.3×10^{10}	
f		(1:6:3)	3.2	8.1	2×10^{14}	8.8×10^{10}	
g		(1:3:3)	2.9	6.0	1×10^{14}	7.4×10^{10}	
h		(1:3:4)	3.0	2.3	9×10^{13}	1.2×10^{11}	
i		$\sim$(15:9:7)	15	$\sim$2.5	$\sim 8 \times 10^{14}$	$\sim 2 \times 10^{11}$ (max)	
IIa	$H_2O + NH_3 + {}^{13}CH_4$	nc[b]	$\sim$2.5	$\sim$1.2	$\sim 7 \times 10^{13}$	$\sim 2 \times 10^{11}$ (max)	
b		nc	$\sim$5.0	$\sim$2.8	$\sim 3 \times 10^{14}$	$\sim 2 \times 10^{11}$ (max)	
c		(20:13:16)	$\sim$24	$\sim$2.6	$\sim 1 \times 10^{15}$	$\sim 2 \times 10^{11}$ (max)	Luminescence: Fig. 6
d		nc	$\sim$5.0	$\sim$1.4	$\sim 3 \times 10^{14}$	$\sim 2 \times 10^{11}$ (max)	
e		nc	$\sim$9.0	$\sim$2.1	$\sim 4 \times 10^{14}$	$\sim 2 \times 10^{11}$ (max)	
f		(1:1:3)	1.7	$\sim$3.9	1×10^{14}	$\sim 2 \times 10^{11}$ (max)	
g		(1:1:4)	1.4	$\sim$3.5	1×10^{14}	$\sim 2 \times 10^{11}$ (max)	
III	$H_2O + N_2 + CH_4$	(1:1:1)[c]	2.8	$\sim$1.5	9×10^{13}	$\sim 2 \times 10^{11}$ (max)	
IV	$H_2O + N_2 + CO_2$	(1:1:1)[c,d]	0.1	$\sim$2.1	5×10^{12}	$\sim 2 \times 10^{11}$ (max)	Spectrum: Fig. 4, Table V
Va	$H_2O + N_2 + CO$	(5:1:1)[c,d]	0.7	$\sim$2.9	5×10^{13}	$\sim 2 \times 10^{11}$ (max)	Spectrum: Fig. 5, Table VI
b	$H_2O + NH_3 + CO$	(2:>1:2)[d]	0.2	$\sim$2.0	1×10^{13}	$\sim 2 \times 10^{11}$ (max)	
c		(2:3:1)	0.4	$\sim$1.0	7×10^{12}	$\sim 2 \times 10^{11}$ (max)	
d		(5:10:1)	0.7	1.8	2×10^{13}	1.3×10^{11}	
VIa	$H_2O + NH_3 + C_3H_8$[e]	(9:5:4)[c]	nc	<4.0	2×10^{14}[f]		Residue: Fig. 7
b		(7:4:3)[c]	nc	<4.0	2×10^{13}[f]		Residue: Fig. 7

[a] Mass ratio approximated by calculating equivalent thickness of each molecular component using appropriate absorption coefficients (unless otherwise noted).

[b] nc, Not calculated.

[c] Ratio measured in gas phase mixture prior to deposition.

[d] Ratio very uncertain.

[e] Proton energy = 1.5 MeV, ice temperature = 77°K.

[f] Incident fluence.

firmed in experiment set II using [^{13}C]methane which resulted in the formation of [^{13}C]carbon dioxide at a rate proportional to the incident flux. A decrease in the CH_4 lines is noticeable in Fig. 3, after irradiation.

Some coloration of the irradiated ice was observed in this and other experiments although not all irradiated films were visually checked for coloration due to the awkward location of the viewing window. When viewed, however, a central circular yellowish area was noticeable where the irradiating beam was most intense; fainter coloration extended over the entire sample. No coloration appeared in a small crescent-shaped area at the edge of the ice film where the thermal radiation shield of the cryostat shadowed the ice from the proton beam.

The volatile fraction of a similarly irradiated ice (set Ih) was collected in a liquid nitrogen-trapped tube as the ice was warmed above 77°K. Gas chromatographic analysis (designed to be most sensitive to the detection of organic compounds C_1–C_{10}) was used to identify CH_4, C_2H_6 or C_2H_4, and C_3H_8 in the ratio 31 : 22 : 1.

The decrease in strength of the ν_4 $^{12}CH_4$ and $^{13}CH_4$ absorption line as a function of fluence was measured quantitatively (set Ia and set IIg, respectively) after an average absorbed fluence of 1.5×10^{14} MeV/cm^2 which is $\sim$19 eV/molecule or half the Oort

TABLE IV

WAVENUMBERS OF NEW ABSORPTION FEATURES AFTER IRRADIATING $H_2O + NH_3 + CH_4$ ICE

cm^{-1}	Identification	Unidentified features (cm^{-1})
2968	C_2H_6	2955
2930	C_2H_6	2260
2875	C_2H_6	2170
2342	CO_2	2100
2282	$^{13}CO_2$	1470
2140	CO	1380
2040	N–N–N species[a]	1340 (broad band)
1460–1453	C_2H_6	
1368	C_2H_6 (?)	
818	C_2H_6	
650	CO_2, (654 and 660 cm^{-1} lines were unresolved)	

[a] Similar to the N–N–N stretch of the ν_2 fundamental of solid NH_4N_3 at 90°K, Dows *et al.* (1955).

cloud dose (see Table II). This is estimated to be equivalent to the energy absorbed in the top 20-cm layer of cometary ice in ~1.5 billion years or to the energy absorbed in a 20-cm layer at a depth of about 1 m in a comet irradiated for 4.5 billion years. A 66% decrease in the line strength of CH_4 occurred. The average CH_4 content before irradiation was 46% by mass.

Substitution of N_2 for NH_3 in the ice mixture was studied in experiment set III. Qualitatively similar results were obtained even though the difference between the bond energies of these molecules is 5.4 eV/molecule. N_2O was identified only in experiment set III.

In the following two experiments (sets IV and Va), CO_2 or CO was used instead of CH_4 as the source of carbon. In these mixtures, N_2 was substituted for NH_3 as a source of nitrogen to circumvent the reaction between NH_3 and CO_2 which results in $(NH_4)NH_2CO_2$. Figure 4 shows the infrared spectrum of an $H_2O + N_2 + CO_2$ ice (set IV) before and after irradiation. A list of new absorption lines observed after irradiation is given in Table V. The intensity of the unidentified lines at 2240, 1260, and 1243 cm^{-1} was observed to decrease when the ice was warmed from 20 to 26°K suggesting that very reactive radical species may be present. Further work is necessary before identification of these reactive species can be made. A decrease in the intensity of the CO_2 line and subsequent increase in the CO line as a function of absorbed fluence was observed. The intensity of the ν_3 CO_2 (2143 cm^{-1}) line decreased ~18% after the ice mixture had absorbed 5×10^{12} MeV/cm^2 which is ~14 eV/molecule or approximately one-third the Oort cloud dose. The CO_2 content before irradiation was 55% by mass.

In set Va, an ice mixture of $H_2O + N_2 + CO$ was irradiated until the absorbed fluence was 4.6×10^{13} MeV/cm^2. The infrared spectrum of this ice, the thickness of which was ≤ 1 μm, is shown in Fig. 5. A list of new absorption lines observed after irradiation is given in Table VI. In addition to the synthesis of CO_2, a small signature tentatively attributed to CH_4 is observed. A decrease in the intensity of the CO absorption line and subsequent increase in the CO_2 absorption line as a function of absorbed fluence was measured (set Vb). The intensity of the CO absorption line decreased ~46% after the ice mixture had absorbed

TABLE V

WAVENUMBERS OF NEW ABSORPTION FEATURES AFTER IRRADIATING $H_2O + N_2 + CO_2$ ICE

cm^{-1}	Identification	Unidentified features (cm^{-1})
2143	^{12}CO	2240[a]
2100	^{13}CO	2180
1870	NO	2050
1303	CH_4	1260[a]
660	CO_2 (654 and 660 cm^{-1} lines were unresolved)	
		1243[a]
		1038

[a] Possibly associated with radical species.

TABLE VI

WAVENUMBERS OF NEW ABSORPTION FEATURES AFTER IRRADIATING $H_2O + N_2 + CO$ ICE

cm^{-1}	Identification	Unidentified features (cm^{-1})
2343	$^{12}CO_2$	2245
2282	$^{13}CO_2$	2240
1300 small	CH_4[a]	2180
650	CO_2 (654 and 660 cm^{-1} lines were unresolved)	1460 (broad band)
		1015

[a] Tentative.

$\sim 5 \times 10^{13}$ MeV/cm^2 which is $\sim$19 eV/molecule or approximately one-half the Oort cloud dose. The average CO content before irradiation was 22% by mass.

In experiment sets IV and V, some small increase in the CO_2 absorption line occurred during irradiation due to CO_2 cryopumped from the unbaked walls of the vacuum system. Because of this CO_2, it was not possible to derive an accurate reaction rate for the synthesis of CO from CO_2, or CO_2 from CO. However, the fact that the new species are formed is not in question. In general, the rate constants for the production in the ice mixture of CO from CO_2, and CO_2 from CO seem to be of the same order of magnitude based on over simplified first-order reactions which do not represent the complex radiation chemistry in the cometary ice mixture. However, if the rate constants (k) are the same order of magnitude [i.e., $k(CO \rightarrow CO_2) \approx k(CO_2 \rightarrow CO)$], then, when either CO or CO_2 is initially present in a primitive comet, nearly equal fractions of both molecules will result due to radiation synthesis in the outer few meters of the comet.

Warmup of Irradiated Ices

During slow warming of an irradiated, thicker $H_2O + NH_3 + {}^{13}CH_4$ ice (set IIc), luminescence was visually detected and photometrically measured. Concurrent pressure enhancements were also recorded. An example of the luminescence and simultaneous pressure bursts observed during warming from 22 to 32°K is given in Fig. 6. Upon recooling to 20°K from 26°K (see A, Fig. 6), luminescent activity was extinguished and did not reoccur until the ice was again warmed to 26°K. While increasing the temperature from 30 to 90°K, the thermoluminescent activity was relatively low but increased again between 90 and 150°K. Within the higher temperature region broader, smoother curves of emission vs time were recorded. A more detailed discussion of the observation of thermoluminescence and the simultaneous pressure bursts is planned for a later paper.

The observation of luminescence in the irradiated ice mixture below 40°K suggests that reactive species formed during irradiation recombine exothermically to produce electronically excited species. These irreversible reactions result in the observed luminescence and pressure enhancements. Although there are several specific mechanisms which could explain the radiation-induced thermoluminescence and concurrent pressure enhancements, there is at present insufficient data on which to choose the mechanisms most important in this experiment. In the case of burst No. 3, Fig. 6, it was estimated that approximately 0.5% of the initial mass of the ice sample was released between 26 and 28°K. Blank samples of unirradiated ices showed some apparent luminescence during warming from 20°K which was not accompanied by pressure bursts. The intensity of the emissions was about one order of magnitude lower than that observed for irradiated ice. These emissions were attributed to light scattered into the photodetector from the gas ionization region of the ion pump.

After warming, all irradiated ice mixtures left a nonvolatile residue on the sample substrate at room temperature. This opaque yellowish film often appeared to have a circular concentration of material where the

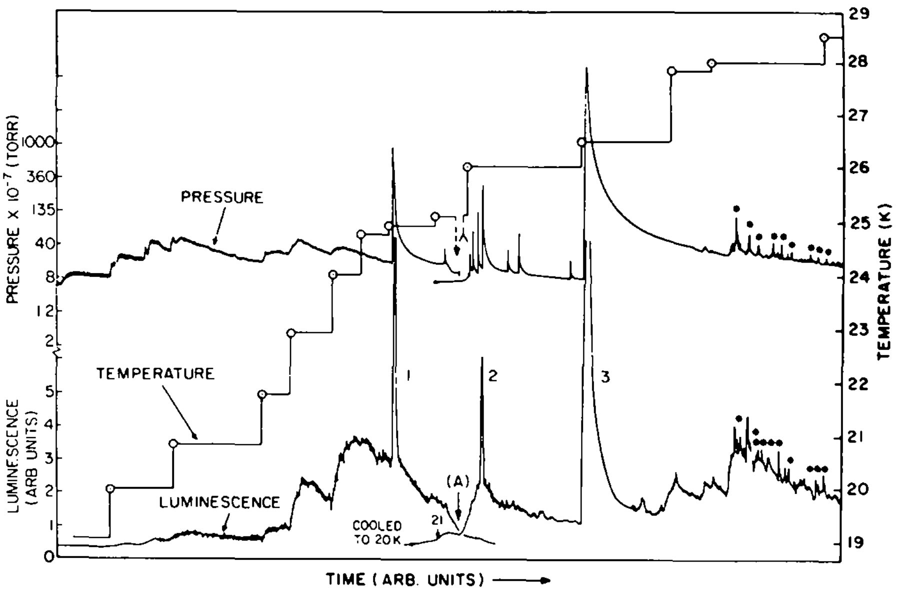

FIG. 6. Luminescence and pressure enhancements in an irradiated $H_2O + NH_3 + CH_4$ ice mixture during incremental warming from $T = 19$ to 28.5°K. In most cases pressure enhancements occur simultaneously with luminescent emissions (e.g., luminescent emissions 1–3). Luminescent emissions and pressure enhancements marked with an asterisk occur while the temperature is constant at ~28°K. These emissions may result from a series of exothermic reactions in the ice.

proton beam was most intense. Since a yellowish coloration was observed in the irradiated ice at 20°K, it is possible that some of the residue material is formed at 20°K. The infrared spectra of several residues (set VIa,b; set Id) are shown in Fig. 7. Dominant absorption features occur near 3.4 and 9.9 μm (see Moore and Donn, 1982, for discussion of the infrared spectrum). Several residues were weighed on a microbalance in order to estimate the quantity of ice converted into residue as the result of irradiation. Using this technique, it was estimated that 0.9 ± 0.2% of the ice mass was converted into a nonvolatile residue after the absorption of an energy density equivalent to 1.7×10^{17} MeV/cm^3. Preliminary gas chromatographic analysis of the residues revealed literally hundreds of organic compounds which were not present in similarly treated blank samples. Amino acid analysis of the residue was inconclusive due to difficulties in separating the water-soluble (containing amino acids) fraction. Luminescent emissions and yellowish residues were also observed in photolyzed interstellar-type ices by Greenberg (1982).

IV. DISCUSSION

Based on our laboratory simulations, we predict that cosmic radiation can significantly reprocess the upper icy layers of new comets over 4.6 billion years. We have listed the various infrared signatures of molecules synthesized at 20°K during proton irradiation (Tables IV–VI). Particularly noticeable, in ice mixtures containing methane, is the decrease in the strength of the ν_4 CH_4 line by 66% for an absorbed energy density believed similar to that at a depth of 1 m in a new comet. An extrapolation of our data to include even higher absorbed energy densities, believed typical of the outer 40-cm ice layer of new comets, suggests that more than 79% of the original methane would have reacted to form a new product. The inner region of a comet will contain a larger fraction of primitive methane since

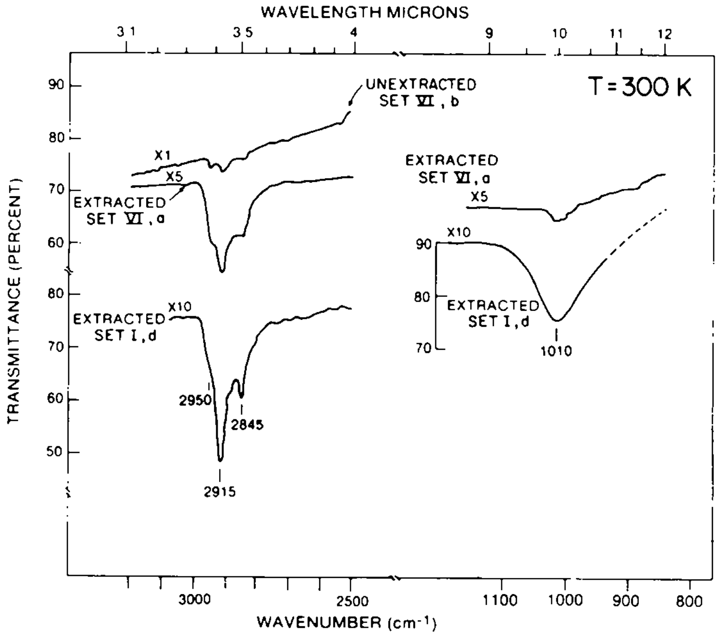

FIG. 7. Infrared spectra of residues from irradiated ice mixtures.

this volume accumulates less cosmic ray energy.

Proton-irradiated ice mixtures containing H_2O and CO, or H_2O and CO_2 resulted in the synthesis of CO_2[3] or CO (respectively) at rates which appear to be approximately similar. This result suggests that CO, concentrated in the outer layers of new comets, may be a significant component of the super-volatile ice required to eject material from the heads of new comets at distances of 15 AU or even larger (distance predicted by Sekanina's calculations, 1973). This volatile layer would be removed during the first perihelion passage resulting in a less active comet during subsequent apparitions. As mentioned earlier this mechanism is postulated as an explanation for the large "disappearance" rate of newer comets.

Since a prominent emission from cometary comae is due to the CN radical, it is interesting to note that no signature of a synthesized CN-bonded molecule was detected in these experiments. The detection in the ice mixture of 1% HCN, for example, would not be possible in our experiments by virtue of the location of HCN's strongest infrared absorption in a region obscured by water, coupled with its weaker absorption coefficient. The detection of molecules containing CN polymers in the room-temperature residue requires techniques more elaborate than those used in this experiment. It is expected, however, that an appreciable concentration of the CN species in the starting mixture would yield an array of interesting biogenic compounds. Further work on the detailed analysis of residues is planned.

Our studies support Whipple's (1977) postulate that the outer layer of a new comet would be a volatile icy frosting containing reactive species formed as the result of cosmic ray irradiation. Although the nature of the reactive species was not determined using infrared techniques (i.e., radical species were not positively identified), irradiated ice mixtures were observed to exhibit luminescence and concurrent pres-

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[3] Irradiation of an $H_2O + NH_3 + {}^{13}CH_4$ ice also produced ${}^{13}CO_2$.

sure enhancements during warming.[4] The luminescence and concurrent release of material we observed in the laboratory would occur when a new cometary nucleus is warmed to 32°K and this could occur at a heliocentric distance of more than 100 AU ($A_v = 0.65$ and $A_{IR} = 0$). Conceivably, emissions could occur at a variety of distances less than 100 AU as cooler subsurface-irradiated ices are warmed through the appropriate temperature interval. This type of exothermic activity, if sufficiently energetic, could result in outbursts of material from new comets at distances beyond those suggested by Sekanina (1973). Above 50°K, the exothermicity of the reactions involved in the thermoluminescence has not been measured quantitatively. Our data suggests that some enhancement in pressure occurs. Although the luminescent emissions could not be directly observed in comets, radiation-induced activities could contribute to the increased brightness and activity in new comets at heliocentric distances between 5.3 and 3 AU if sufficient material is released as the result of corresponding pressure enhancements. Another possible contribution to the increased activity of new comets at this distance is an exothermic event associated with the phase changes of water (e.g., Patashnick *et al.*, 1974; Smoluchowski, 1981). The magnitude of the radiation induced contribution would decrease with successive returns of the comet to perihelion as deeper, less irradiated ices were exposed.

The results of our experiments also support Donn's (1976) postulate that cosmic ray radiation would tend to polymerize the simple volatile molecules resulting in a less volatile material. In our laboratory simulations, approximately 1% of the volatile ice mass was converted into a complicated nonvolatile residue. The energy density absorbed in our experimental ices is the same as the estimated absorbed energy density in a new cometary nucleus at a depth of approximately 1 to 2 m. An even larger absorbed energy density occurs near the cometary surface. Using the calculated mass conversion rate of ~1% we find that a comet with a 10-km radius could accumulate in its outer 2 m, 2.3×10^{10} kg (over 10 million tons) of residue in 4.6 billion years.

During vaporization of ices from the surface of a comet, some fraction of a similar nonvolatile residue is expected to remain on the underlying material. This organic residue would result in the formation, to some degree, of an inert, chemical-insulating coating on the underlying ice. Cometary observations indicate a decrease in activity in comets from the upper mantle to the core (Whipple, 1977). This could be explained as a systematic change in the composition or volatility of the material, or as an increase in cohesiveness of the material. On the other hand, during vaporization of ices from the cometary surface, some of the residue is probably carried into the coma. This material could be a source of complex organic compounds in the solar system.

V. SUMMARY

Laboratory Observations

1. New molecular species were synthesized in the solid phase in cometary-type ice mixtures as a result of proton irradiation at 20°K. The synthesized molecules identified were: C_2H_6, CO_2, CO, N_2O, NO, and CH_4 (weak).

a. Proton irradiation of ice mixtures containing CH_4 and H_2O resulted in the synthesis of CO_2. When CH_4 was 46% of the initial ice mixture, more than two-thirds of the methane was depleted due to its conversion into other molecules. The energy density absorbed during these experiments was comparable to the estimated accumulated energy density at a depth of ~1 meter in a new cometary nucleus.

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[4] The experimental results are for irradiation of compact, condensed gases in the form of ice. The outer layers of a new comet are more likely to be a low-density snow (Donn, 1963). There is little experimental work on such material.

b. Proton irradiation of ice mixtures containing CO and H_2O resulted in the synthesis of CO_2; those containing CO_2 and H_2O resulted in the synthesis of CO. The rate constants for these solid phase reactions seem to be of the same order of magnitude and under these conditions new comets would have nearly equal fractions of CO and CO_2 in their outer layer if either is initially present.

2. During warming, irradiated ice mixtures exhibited thermoluminescent activity and concurrent pressure enhancements. This activity was most intense between 20 and 32°K, and 100 to 150°K. These temperature ranges roughly correspond to comets at solar distances $r > 100$ AU, and $r = 2$–5 AU, respectively.

3. Coloration of the irradiated ice was observed at 20°K. Coloration implies a change in the visual albedo of the cometary surface ice as a result of proton irradiation.

4. In irradiated ice mixtures approximately 1% of the volatile ice mass was converted into a nonvolatile residue. The nonvolatile residue contained hundreds of new carbon-containing compounds not present in blank samples.

Cometary Implications

1. It is suggested by our laboratory observations that outbursts of new comets beginning at distances up to perhaps 100 AU are due to the release of radiation-synthesized material as the ice is warmed to 32°K. Observations of new comets at very large distances may detect these activities, or the result of these activities (i.e., the observation of remnant particle tails).

2. Based on our laboratory experiments, new comets are expected to contain the largest fraction of nonprimitive (synthesized) molecules within their outer few meters. New comets are also predicted to have a significant depletion of methane in their outer layers compared to their inner volume of ice, or compared to more evolved comets. During vaporization and ionization of the outer ice layer of a new comet, a different ion and molecular concentration will result in the coma than for the similar passage of a more evolved comet. Gas chromatographic–mass spectrometric measurements from a rendezvous satellite through the coma of comets of different ages could measure these concentrations. Such measurements could also be made by sufficiently sensitive infrared spectroscopy in the 2.5- to 15-μm region.

3. More viable studies would include spectroscopic observations of the nucleus at large heliocentric distances, pre- and post perihelion for comets of different ages. Equipment to do this should be available in the not too distant future.

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