

Ice Chemistry on the Galilean Satellites

by

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Abstract

Jupiter's icy satellites Europa, Ganymede and Callisto are subject to energy fluxes from electrons, photons and magnetospheric plasma ion bombardment. As water ice and CO₂ ice are thought to be present on their surfaces, the radiolysis of these materials over time should produce more complicated CHO-containing molecules. These may include: CH₃OH, H₂CO, CH₂CO, C₃O₂, HCOOH, CH₃COOH, H₂CO₃, HCOOCH, (CH₃)₂CO, CH₃CH₂OH, HOCH₂CH₂OH, polymeric C₃O₂ and polymeric H₂CO (POM). The water fragmentation products OH, O₂, HO₂, H₂O₂, and O₃ should also be produced. The molecules formed should be detectable with ground-based instruments because of their many active infra-red bands. Another product produced is CO, which will have a high vapor pressure over a Galilean satellite surface at typical temperatures. The vapor pressure of CO at the nighttime temperature of 70 K could be as high as 150 millibar. Ganymede's unique dipolar magnetic field should induce more chemistry in its polar regions due to the focusing of radiation to higher latitudes. The observed lack of leading/trailing asymmetry in its SO₂ absorption correlates with this redirection of plasma ions towards the poles. The observance of O atom emissions at high latitudes by Hall *et al.* (1998) is also consistent with this picture. The ratio of plasma energies directed to the poles to those directed to the equatorial regions is ~ 4.

ices

magnetosphere

chemistry

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Introduction

Outer planet satellites live in high-radiation environments. Planetary magnetospheres in which they are immersed are populated by energetic particles which cause chemical and physical changes in their surfaces. The presence of carbon dioxide was detected on the surfaces of the satellites Ganymede and Callisto by the Galileo NIMS instrument (Carlson *et al.* 1996) and may occur also on Europa. This molecule was inferred from the 4.25 μm band seen in the infrared spectrum. As water ice was already known to be present there, its combination with CO_2 ice was recognized to be a potent mixture for chemical evolution on these satellites (Delitsky and Lane, 1997). Subject to continuous plasma bombardment from the Jovian magnetosphere, as well as solar wind particles, UV radiation and cosmic rays, these ices will react to form new CHO-containing products, which then undergo thermal evolution from the natural day/night cycles of these tidally-locked satellites. As radiation causes the disruption of the crystalline structure of ices, H_2O would evolve under the magnetospheric onslaught from a cubic or hexagonal structure (under typical Jovian temperature conditions) to an amorphous structure (Strazzulla *et al.* 1992, Hudson and Moore 1995). Water ice is typically amorphous when deposited below 110 K, but it can be driven to become amorphous (from being crystalline) above this temperature by radiation. However, Radiation Amorphizes, but Heat Crystallizes: the plasma radiation amorphizes the crystalline structure by disrupting the ordering of molecules and creating voids and holes in the ice, causing it to become non-crystalline, while the day/night cycles reheat them and cause recrystallization. Reactions are facilitated in non-crystalline amorphous or liquid domains. Chemistry will be occurring all of the time from the plasma bombardment, but heating effects, which will drive radicals and volatiles out of the lattice will also occur as the satellite revolves around Jupiter, with only one hemisphere being in sunlight. Ganymede's recently discovered magnetic field may in fact direct plasma ions into the polar regions and cause ice chemistry that will remain unaffected by thermal effects (Kivelson *et al.* 1996, 1997a). In this paper, we characterize the chemistry on the surfaces of Europa, Ganymede and Callisto that results from continuous plasma bombardment of $\text{H}_2\text{O}/\text{CO}_2$ ices, as well as consider magnetospheric energy flux changes from Voyager to Galileo era, and how Ganymede's unique magnetic field shape redirects energy to its polar regions causing hemispherical differences in chemistry and spectral properties.

Magnetospheres

Jupiter's magnetosphere is known to contain populations of plasma ions bound to its magnetic field lines. The plasma populations consist of the following ions:

O^+ , O^{2+} , O^{3+} , O^{4+} , S^+ , S^{2+} , S^{3+} , S^{4+} , S^{5+} , S_2^+ , SO_2^+ , Na^+ , K^{2+} , C^{6+} , H_2O^+ , H_3O^+ , OH^+ , H^+ , He^+ , H_2^+ and H_3^+ . The oxygen, sulfur, sodium and potassium species arise from Io volcanic emissions which release tons of material per minute into the magnetosphere. O^+ and S^+ are the most abundant magnetospheric plasma ions by number (Dessler 1983). Water group ions (H_2O^+ , H_3O^+) come from sputtering of the water ice surfaces on Europa, Ganymede and Callisto (Geiss *et al.* 1992). Species such as H^+ , He^+ , O^{6+} and C^{6+} are from the solar wind. Jupiter's ionosphere supply the H^+ , H_2^+ , and H_3^+ . These species will impact the surfaces of the Galilean satellites as these bodies revolve around Jupiter. Some species implant into the ice and cause chemical reactions with themselves (Lane *et al.* 1981). Others break chemical bonds and re-sort the atoms in the molecules that are present, creating new chemical species.

Ganymede was found to be the first satellite containing its own magnetosphere (Kivelson *et al.* 1996, 1997a, Williams *et al.* 1997). The shape of the magnetosphere is unusual; it has open field lines connecting to the polar regions down to $\sim 45^\circ$ latitude. Between 45° N - 45° S, there are closed field lines that approximate a 'spare tire' in shape around the middle of Ganymede. The effect of this shape is to focus charged particles from Jupiter's magnetosphere into the polar regions of Ganymede, except for those energetic enough to bypass the field lines in the equatorial region and reach the surface. The cutoff for energetic particles that do not reach the equatorial surface is thought to be ~ 100 keV (J. Cooper, A. Eviatar, personal communications, 1998). Particles with energies less than 100 keV will be swept up towards the poles along Ganymede's open field lines and impact the surface there. See Figure 1.

For Europa, the magnetic field shape is not yet fully known, but the magnetic field strength is very variable and complex. The Jovian magnetic field strength near Europa is around 400 - 470 nT, whereas the field strength of Europa was detected as being as high as 770 nT on Galileo's E12 orbit, and shows a pile-up of the field upstream from Europa, and a decrease of the field downstream from Europa (M. Kivelson, personal communication, 1998). The effect on plasma deposition may also be unusual. A tilt of 135° to the rotation axis for the dipole field was the best fit to the first Europa pass (Kivelson *et al.* 1997b). This fit may be revised after later Europa encounters. The topology of the plasma flow is not yet fully elucidated. Most probably, the field is too weak to have much effect on plasma redirection.

Callisto is believed to have no intrinsic magnetic field (Khurana *et al.* 1997). This implies that the magnetospheric ions have access to the equatorial regions as in the case of a non-magnetized body. The magnetospheric plasma bound to the Jovian magnetic field lines rotates with the 10 hour Jupiter rotation period. This is much faster than the orbital period of the satellites, and so the bound plasma catches up to the satellites during their orbit around Jupiter and impacts their surfaces on their trailing sides. Given this process, hemispheric asymmetries in chemistry are expected.

Ice Physics

Europa, Ganymede and Callisto have temperatures ranging from 70-180 K on their surfaces (Squyres 1980, Urquhart and Jakosky 1996). These temperatures range over the different crystalline forms of water ice. Water ice has a hexagonal structure above 150 K, and a cubic crystalline structure between 110 - 150 K. Below 110 K, water has an amorphous non-crystalline structure (Hobbs, 1974, Leto, *et al.* 1996). When heated, amorphous ice changes into crystalline ice.

Plasma irradiation of ice will convert it from crystalline to amorphous over short timescales. As Strazzulla *et al.* (1992) found in their ion-beam induced amorphization experiments with water ice, there are no dose rate effects. The fraction of ice converted from cubic crystalline structure to amorphous depends only on the total amount of energy deposited, not on the irradiation rate. Therefore, we can estimate for each region the amount of irradiation products that would be obtained, based on energy input.

Ultraviolet radiation will also amorphize water ice (Kouchi and Koroda 1990). Water will stay crystalline when cooled down if nothing happens to it (i.e. it is not subjected to radiation), even if it is cooled down to temperatures where water ice is normally amorphous when it is condensed from the gas phase (below ~110 K)

When water is recrystallized by heating, the surface layers will retain some disorder because of 'dangling' H atoms, which promote reactions. This is because the disordered surface molecules can be accessed at a lower energy cost than those in the interior of the crystal which facilitates reactions of adsorbed molecules (Devlin and Buch 1997).

A significant effect of temperature on the chemistry is related to the mobility in water ice of OH radicals. OH formed within water-ice structures is immobile below temperatures of 95 K (Siegel *et al.* 1961, Johnson and Quickenden 1997) and is free to migrate within the ice lattice at temperatures approaching 110 K. Any OH formed on the sunlit side of each of these

satellites will be active and participate in chemical reactions until such time as the temperature drops below 95 K. At that point OH reactions drastically diminish.

Here, we use the term 'poles' interchangeably with 'polar region' which we consider to be the region between 45 - 90 ° N or S latitude. 'Equatorial regions' (or 'equator') refers to that region between 45 ° N and 45 ° S on the satellites.

Chemistry of mixed ices

If CO₂ is mixed in with H₂O ice, it may be in a clathrate form or other occluded state, and could occupy 2 different kinds of sites in a lattice. The 2 different sites are 'interstitial' sites, where the CO₂ is caught in between two regularly spaced H₂O molecules, or 'substitutional' sites where CO₂ takes the place of a regular H₂O molecule in the lattice (Palumbo and Strazzulla 1993). As an example of this type of arrangement, in a H₂O/CO mixed ice, the interstitial CO molecules are responsible for the 2152 cm⁻¹ band seen in the IR spectrum and the substitutional CO cause the 2139 cm⁻¹ band. As the mixture is warmed up, the 2152 cm⁻¹ band starts to decrease and then disappear as the CO is forced out of interstitial sites by the crystallization (Sandford *et al.*, 1988, Palumbo and Strazzulla 1993).

If an amorphous water ice containing CO₂, or the products of the plasma radiolysis of a H₂O/CO₂ ice, is heated (as will occur when the satellite is in sunlight), volatile products (such as CO) produced by the plasma bombardment will then be driven off by the thermal cycling as the water ice attempts to recrystallize at the higher temperatures (Schmitt *et al.* 1989, Brucato *et al.* 1997a) leaving the more refractory residual materials. Absorbances in the IR for CO, which occur upon bombardment of H₂O/CO₂ ice with plasma ions, disappear upon warmup of the ices above 157 K (Brucato *et al.*, 1997b). However, irradiation of these ices will actually preserve the presence of CO and CO₂ above their normal sublimation temperatures (Hudson and Donn, 1991). Brucato *et al.* (1997b) found that CO and CO₂ were still present in their irradiated ice films at 97 and 157 K, even though CO typically sublimates at 30 K. CO₂ sublimates at 72 K. Upon heating their ice films to 247 K, only H₂CO₃ remained. These temperatures of 97 - 157 K are within the range of temperatures occurring on the Galilean satellites.

Hage *et al.* (1998) confirm the kinetic stability of H₂CO₃ as well as pointing out that some of its infrared bands occur in the 3.4 -3.88 μm region and could contribute to absorptions observed in Galileo NIMS spectra of Ganymede and Callisto (Carlson *et al.* 1996). A band at 3.88 μm was indeed noted in NIMS

spectra (McCord *et al.* 1997) and attributed to an -S-H bond stretch. Possibly H_2CO_3 is a more likely candidate, given the increasing belief in the $4.25 \mu\text{m}$ band as being due to the presence of CO_2 .

The stabilization of volatiles above their normal sublimation temperatures occurs because the CO , CO_2 and other fragmentary products of the irradiation will be hydrogen-bonded to the water ice in the matrix and be unable to simply volatilize and leave the matrix at the normal temperature. Volatilization from a heterogeneous mixture requires more energy than when the material is in a pure state (Hagen 1983, Ratcliffe and Ripmeester 1986). These hydrogen bonding effects will be a counteracting force to the crystallization mechanism that comes from heating, serving to hold the products of irradiation longer in the voids. In a more inert matrix, where these forces are not operational, irradiation products would be more likely to escape at their normal temperatures.

Typical species that have been seen in various laboratory experiments from radiolysis of $\text{H}_2\text{O}/\text{CO}_2$ ice are: H_2CO (formaldehyde), CO , CH_2CO (ketene), OH , C_3O_2 (carbon suboxide), CO_3 , O_3 , H_2CO_3 (carbonic acid), CH_4 , HCO , O_2 , HO_2 , H_2O_2 , and CO_3 (Benit *et al.* 1988, Baratta *et al.* 1994, Strazzulla *et al.* 1995a, DelloRusso *et al.* 1993, Moore and Khanna, 1991). Once H_2CO is produced, further radiolysis of $\text{H}_2\text{CO}/\text{H}_2\text{O}$ will yield methanol, CH_3OH (Gerakines, *et al.* 1996, Schutte *et al.* 1996). Methanol also originates from mixtures where the starting materials are $\text{H}_2\text{O}/\text{CO}$ (Moore, *et al.* 1991). (As CO is one of the products of $\text{H}_2\text{O}/\text{CO}_2$ radiolysis, methanol may be a secondary product from $\text{H}_2\text{O}/\text{CO}_2$). Further radiolysis of $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ may then yield other products: HCO and H_2CO (Moore *et al.* 1996) and possibly acetone $(\text{CH}_3)_2\text{CO}$ (Baratta *et al.* 1994, Strazzulla *et al.* 1995b). (The presence of acetone was suggested from 4 bands in the IR by Baratta *et al.* 1994, but has not been positively identified or confirmed by other experimenters.) Reaction of H_2CO with the abundant OH radicals (that will be present in the ice from water fragmentation) will yield HCO . If an HCO radical reacts with another HCO , then glyoxal, HCOOCH , is formed. (Its structure is $\text{H}(\text{C}=\text{O})-(\text{C}=\text{O})\text{H}$). It is more likely however that the HCO would encounter an OH radical, which reacts with HCO to yield formic acid, HCOOH (Tidwell, 1997). Formic acid is another possible product from radiolysis of $\text{H}_2\text{O}/\text{CO}$ ices, and may occur from methanol/water radiolysis (Moore *et al.*, 1996). (An IR band seen there at 1713 cm^{-1} may be from HCOOH , but since this band is due to a $\text{C}=\text{O}$ stretch, it can also originate from other $\text{C}=\text{O}$ containing molecules. The presence of HCOOH needs to be confirmed with further laboratory work.)

Pure CO yields C_3O_2 (carbon suboxide) upon radiolysis (Sugimoto *et al.* 1986, Anderson *et al.*, 1965), which after sufficient energy input will polymerize, to $(\text{C}_3\text{O}_2)_n$ (Smith *et al.* 1963, Briggs *et al.* 1968). So will formaldehyde H_2CO ; its

polymer is polyoxymethylene, or 'POM' ($-\text{OCH}_2\text{OCH}_2\text{O}-$). Ketene, CH_2CO , upon reaction with water yields acetic acid, CH_3COOH (Bothe *et al* 1980, Allen *et al* 1995), but if it reacts with OH instead (creating a HOCH_2CO radical), this can then decompose to HOCH_2 radical and CO (Tidwell, 1997). HOCH_2 can also form from radiolysis of CH_3OH (Hudson and Moore 1995). If HOCH_2 reacts with another HOCH_2 , the product is ethylene glycol, $\text{HOCH}_2\text{CH}_2\text{OH}$ (Hudson and Moore 1995). This molecule was seen in irradiation experiments of $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ mixtures, along with another 2-carbon molecule, ethanol, $\text{CH}_3\text{CH}_2\text{OH}$ (Moore *et al* 1996).

Some products listed here have stronger confirmation than others. The presence of ketene was inferred from 6 bands in the IR in the paper by Benit *et al.* (1988). However, not all of the bands were seen by other experimentalists. Therefore, additional work is needed to confirm the presence of this very important intermediate product. Also, acetone's presence is suggested by the 1713 cm^{-1} band and the 530 cm^{-1} band seen by Moore *et al.* 1996. Baratta *et al.* 1994 saw 4 bands ($1720, 1444, 1232$ and 1090 cm^{-1}) that suggested acetone, but the spectral fit is not perfect. The identification of ketene, acetone and their byproducts is therefore somewhat more tentative and needs to be explored with further experimental work.

Figure 2 illustrates these possible reaction pathways of products originating from radiolysis of $\text{H}_2\text{O}/\text{CO}_2$. These paths will occur in 2 component systems, and if many products are present, this may complicate the chemistry. However, figure 2 is designed to suggest molecules that might be considered by observers as possible constituents of the satellite surfaces, because most have been seen in laboratory experiments of solid-state radiolysis of H_2O with other CHO-containing molecules.

Other species present on the satellites will arise from implant chemistry of S^+ and O^+ impacting the $\text{H}_2\text{O}/\text{CO}_2$ surface and creating SO , SO_2 , SO_3 and other materials (Delitsky and Lane 1997).

Radiation and its effects on ices

Figure 3, from the classic book on radiation damage in crystals by Chadderton and Torrens (1969), demonstrates how holes and voids resulting from dislocation of atoms occur in a lattice from impact of an incoming energetic plasma ion. Radiation damage of ices will have multiple effects. Dislocations of molecules as well as electronic excitations can create lattice voids. Whipple (1978), in his studies of ices of comets stated that "for cometary material one might expect not only that usual lattice displacement of atoms and lattice defects in crystals, but also the production of radicals from the molecules. Furthermore, some loss of mobile atoms such as H should

occur and a considerable amount of chemical transformation take place." Cometary ices are subject to an array of radiation effects all of the time which initiate solid-state chemical reactions (Delitsky 1980) and these effects are similar to those that will occur on the Galilean satellites.

For the purposes of this discussion, we will consider water ice to be acting like an oxygen atom lattice, as far as an impacting ion is concerned. In general, as incoming plasma ions at high energy travel through a lattice, they will excite the electron cloud of the molecules along the track and cause vibration, dissociation and dislocation of atoms as they lose energy along their path. Most of the energy deposited will be from this electron excitation (R.E. Johnson, personal communication, 1998). When they have lost energy beyond a certain threshold, then they will act as billiard balls and hit atoms (such as the oxygen atom in water) imparting momentum energy. These plasma ions that impact may hit an atom (called a "knock-on atom") and either make it vibrate in its lattice position but not displace it, or displace it, causing it to hit other atoms in the lattice. The first interaction where vibration is initiated but no atoms are displaced is called a thermal spike or temperature spike. The atom is hit, but gains an energy less than the energy that would be needed to displace it (E_d), so it begins to vibrate in its potential well. The vibration of the knock-on then affects its neighbors, making a local excitation similar to the way it would be if that small region of the solid were raised to a high temperature. This heating will only last a short time (small fractions of a second) but may be effectively as high as 10,000 °K, during which bonds are broken (by molecules getting excited to a repulsive state and dissociating) and radicals are formed. If the primary particle hits a knock-on atom and imparts an energy greater than its displacement energy (E_d), the knock-on will move and hit other atoms in the lattice along its cylindrical path, creating a shower of secondary displacements which will be knocked into interstitial positions. This effect is called a Brinkman displacement spike. See Figure 3. This many interstitials in a lattice would be quite unstable, and so the vacated region would collapse back, refilling the areas, but leaving some holes and misoriented regions. Atoms may bounce some distance from their original places, leaving "depleted zones". There may be single vacancies as well; the largest zones depleted of atoms would be at the end of the track. This gives a lattice at a higher energy (and entropy) than before. The vacated holes provide a location for a micro-atmosphere to form.

Chemical species will have vapor pressures in these micro-atmospheres determined by the temperature in the ice. Products of reactions can deposit on the 'wall' of these voids. Reaction could happen in the gas phase in these micro-atmospheres, or while molecules are adsorbed on the walls. Atoms or molecules in excited states may be quenched by encountering the wall and so may or may not be available for reaction in that more energetic state.

For electron energy deposition, most displacements will occur by electronic excitation; some will be from direct impact. The rate that displaced atoms are generated is given in Unwin and Mugurama (1972) as: $G = n\sigma\phi N$, where n equals the number of atoms/cm³, σ is the total scattering cross section, ϕ is the impacting energetic particle dose rate, and N is the number of secondary displacements. For H₂O, they use an n of 3×10^{22} atoms/cm³ for the oxygen atoms. They also calculate the number of secondary displacements as $N = 1 + \ln E_m/2E_d$ where E_m is the maximum energy transferred to the atom. If an electron hits an oxygen in H₂O, it will transfer less energy than if it hits a hydrogen atom in the H₂O molecule, because of the relative mass. For 100 keV electron impacts, Unwin and Mugurama found that the rate of displaced atoms, G , was on the order of 1.8×10^{18} atoms/cm³ sec for a dose rate of 5×10^{16} electrons/cm² sec, and N was 2 secondary displacements for oxygen atoms, 6 for hydrogen (as these are much lighter and easier to move). On Ganymede, for example, the electron energy flux is given as being ~ 1 erg/cm² sec by Frank *et al.* (1997). This is equal to 6×10^8 keV/cm²sec. Since the range of energies for the electrons are 0.5 - 3.0 keV, if we divide the energy flux by the energy for the electrons of 3 keV, we obtain an electron flux of 2×10^8 electrons/cm² sec. At this energy, electrons cause displacements by electronic excitations. Therefore, if the scattering coefficient for 3 keV and 100 keV electrons are similar, then the rate of displacement of atoms will be on the order of 10^{10} atoms/cm³ sec or less.

Matrix Effects

Hallamasek *et al.* (1997), in studying interstitial and annealed crystal structures, found that 'cryogenic matrices originating from gas phase deposition are, in general, microcrystalline porous solids which may even contain amorphous or nearly amorphous domains'. If crystalline water ice occurs in this form on Ganymede's surface, for example, and CO₂ condenses on its porous surface from a temperature drop during night-time, it may be trapped in a pore when the water ice is reheated during the day. The CO₂ molecules may contribute vibrational energy into this porous structure, which could initiate local melting in the domains where they reside, and cause the formation of amorphous regions as the water anneals into a solid.

In Calvin *et al.* (1995, 1996), the O₂ bands in their spectra of Ganymede are characteristic of liquid or solid O₂ where the O₂ molecules 'see' each other and appear spectrally as dimers. They may occur in domains such as those inside the water ice matrix. As pointed out by Pincock (1969), frozen solutions may be 99 % solid but the liquid holes that are as yet unsolidified have extremely concentrated solutions of reactants, which speeds up reaction time accordingly. Reactions may be catalyzed by near-frozen conditions, and they actually could slow down when thawed out. Molecules in a liquid state have time between collisions that enables vibrational energy to be redistributed

within their bonds in many degrees of freedom. If the molecules contact a crystalline lattice and momentarily remain in the close vicinity of the lattice, a different regime of energy exchange is possible. The lattice enables energy to be transferred to it from the contacting molecule and excited state energy can be diffused among many well-coupled modes in the lattice. Also, if the lattice, by electrostatic attraction to the contacting molecule can cause configurational changes in the 'loosely bound' molecule, this results in increased energy content for that molecule once it leaves the contacted lattice site, enhancing its reactivity. As an example, if CO₂ in a void approaches or contacts the lattice, it may gain some vibrational energy from the contact that would change it from a linear (lowest-energy-state) form into a bent configuration that is at a higher vibrational energy level (i.e. it would be higher up on the potential energy diagram). This extra energy could facilitate further reactions.

In a multicomponent system, the lowest temperature where liquid can exist may be far below the freezing point of the dominant material. In a 2 component system, for example, the system will only be completely solid below the eutectic point (minimum freezing point of the mixture). Between this minimum and the freezing point of the materials, one or the other material could have liquid domains, and so may be spectrally identified as being in the liquid or solid phase (Pincock 1969). For example, O₃ is normally liquid between 80 - 162 K (at 1 atm pressure) and so would remain liquid under satellite conditions in pores where pressure inside can build up (to near 1 atm). Temperatures at the poles on Ganymede get down to 70 K, and so O₃ is more likely solid there which may help explain the latitudinal differences seen in absorbances (Calvin and Spencer 1998).

In a study of water-rich ices containing CO₂ and CO, Schmitt *et al.* (1989) found that crystallization times for amorphous water ice drop precipitously between 100 K and 150 K, which is the normal range of temperatures that may occur on Ganymede and Callisto in their day/night cycles. The equation for crystallization time is given as:

$t_c = A \exp(-E_A/kT)$, where $A = 2.65 \times 10^{-17}$ hour, and $-E/k$ is the activation energy, with $-E/k = 5370$ K. Their Figure 6 shows that depletion of CO or CO₂ from the lattice by diffusion parallels this sharp drop with temperature. For example, crystallization time for water ice at 140 K (a warm day on Ganymede at the equator) is about 1 hour. Depletion time at that temperature is given as slightly longer than this (as the crystallization process squeezes CO or CO₂ out of the water lattice). The time for crystallization increases to ~ 700 hours at 120 K and is on the order of 2×10^5 YEARS at 90 K. (For the lowest temperature at the poles of 70 K, we get the unfathomable time of ~ 6.2 trillion years). Therefore, small molecules and radicals will stay in the lattice in the polar regions for long periods of time and be available for reactions (although the effect of cold temperatures will be to slow chemical reactions

down somewhat) whereas in an equatorial region, with sunlight shining on it, radicals or small molecules may be driven out of the solid and may form atmospheres or other condensing products.

Regional Effects

There are different effects operating on different regions of the satellites. On Ganymede, polar regions see electrons and magnetospheric plasma ions as their energy source. This region also stays dark most of the time as there are few visible and UV photons falling on it. The equatorial regions see both photons from the sun and some magnetospheric plasma ion deposition, and very little electrons. Therefore, there are 2 different energy input regimes to consider.

Squyres (1980) studied the changes with temperature that occur on the Galilean satellites using Voyager data. He shows that the polar regions have very little variation in temperature. See Figure 4. It is seen that if one were at 80° north latitude on Ganymede, for example, that the temperature would stay very cold, varying only from about 70 to 80 K over the course of a Ganymede day (which is about 170 hours (7.1 Earth days)). Any water ice present will likely be amorphous, because it will be subjected to plasma radiation from the magnetosphere, as well as electrons (Barth *et al.* 1997). It will see almost no solar energy, so there may be little effect from UV photons. Therefore, if we have an amorphous water ice with CO_2 present there, the $\text{H}_2\text{O}/\text{CO}_2$ irradiation products will persist and most likely form larger molecules, such as C_3O_2 , H_2CO_3 , H_2CO , CH_3OH , etc. (Barratta *et al.* 1994, Delitsky and Lane 1997). No heating will occur to recrystallize the ice and force out the reacting radicals and molecules. They will persist and recombine over time, their products preserved in deep freeze.

The equatorial regions have somewhat different effects imposed on them. Magnetospheric radiation is primarily deposited in satellites on the equatorial regions on the trailing side, for satellites that do not possess a significant magnetic field. This is likely the case for Europa and Callisto. This occurs because satellites revolve around Jupiter slowly relative to the speed of the magnetosphere, which is tied to Jupiter's rotation period of 10 hours. For Ganymede, the poles receive the most amount of plasma. The equatorial region only experiences the highest energy particles which are much lower in number than the low-energy plasma ions that impact the poles. The energy cutoff is ~ 100 keV (Cooper *et al.* 1997a,b)

For Europa, a hemispheric difference for absorption near 2800 Å has been noted between the trailing and leading sides, from implanting of ions, such as sulfur S^+ , on the trailing side (Lane *et al.* 1981). No hemispheric difference for

this absorption is seen on Ganymede, because of the deflection of most of the ions towards the poles. This correlates with the magnetic field data, implying that the equatorial regions are indeed protected from most of the low and middle energy particle bombardment.

The effect of amorphizing water ice at night in the equatorial regions will be more important on Callisto than on Ganymede or Europa, As Callisto has a slower rotation period than Ganymede (16.5 days versus 7.1 days), its regions stay in nighttime longer. Hudson and Moore (1995) studied how radiation-induced amorphization under proton bombardment decreased as temperature is raised in water ice. They found that a large portion of water ice is amorphized at 13 K, but very little can be amorphized at 77 K. Strazzulla *et al* (1992) used a higher dose of helium ions (which are heavier than protons and will do more ice damage per ion) and found that 25% of the ice was amorphized at 100 K, but 60% could be made amorphous at 77 K. The heavier plasma ions in the magnetosphere will be even more effective in amorphizing ice than helium ions, making this effect more likely on Callisto than during the shorter nights on Europa and Ganymede.

At the equator on Ganymede, the temperature goes from about 90 K to 150 K over a 45 hour period as a given point moves from the dawn terminator to the subsolar point. It stays at temperatures of ~120-150K for between 65-70 hours (see Figure 4). Transformation of water ice from amorphous to crystalline will be accelerated as the temperature rises. Since it takes only tens of seconds for ice to convert from an amorphous to cubic structure at 150 K (Strazzulla *et al* . 1992), the ice sitting in sunlight for 70 hours at the subsolar point (which was caused to be amorphous by the plasma bombardment) will then crystallize. This will have the effect of causing any radical products or small molecules that formed to become more mobile in the ice, and be driven out of the crystal as it's forming. This 'bake-out' of smaller molecules that is occurring should change the carbon chain-length distribution of the molecules formed there, and be somewhat different from those in the polar regions. The fate of these molecules will depend on their melting points and vapor pressures. If CO is formed from H₂O/CO₂ processing, it would have a fairly large vapor pressure above a 150 K surface. CO will then be forming a transient atmosphere for that 70 hours during daylight. As that point goes into nighttime, the vapor pressure of the CO will drop from the temperature change.

Daytime length varies. On Europa, the daytime is about 35 hours long; on Ganymede it is 70 hours, and on Callisto, it is about 170 hr. Europa temperatures range from 70 K to 120 K, Ganymede's from 80 - 150 K, and Callisto's from 70 -180 K (Squyres 1980). Galileo temperature measurements agree within ~ 10 K with this ranges (Orton *et al*. 1996). Visible albedo of each satellite differs significantly from 0.6 for Europa to 0.25 for Callisto. The actual local temperature depends on the thermal inertia of the materials on the

surface (Urquhart and Jakosky 1996). Certain processes will be facilitated dramatically at higher temperatures. This might be one reason that Callisto's surface is so much darker than the other icy satellites.

Heating also affects the micropores in the ice. The micropores will contain micro-atmospheres whose compositions change with time. Pores eventually migrate to the grain boundaries, if there is a thermal gradient across the ice. Warm gas moves towards the cold end of the pore, condensing out and making a new 'wall' of the pore. In this way, the pore will eventually reach the surface and release its contents. Any processed molecules can then escape (Smoluchowski and McWilliam 1984). This could be the way CO would be released.

The effect of this temperature change then is to act as a 'pumping mechanism' that forces the plasma bombardment products out of the ice lattice, to form their own crystal structures which condense on the surface, or become part of a transient daytime atmosphere.

Satellite atmospheres

An atomic hydrogen atmosphere was in fact recently reported to be observed around Ganymede by Barth *et al.* (1997). They give a surface density for H atoms as being 1.5×10^4 atoms/cm³. They suggest 3 mechanisms for the formation of the H atoms detected. These are: 1) photodissociation of water vapor that has sublimated from the surface into H and OH, 2) sputtering of H atoms directly from the surface ice by plasma ions, or 3) photodesorption and ejection of H atoms from water ice by UV photons. In their first mechanism, the OH is thought to recondense on the surface and form oxygen-containing molecules.

It is more likely that the OH stays in the lattice after dissociation of H₂O from the plasma bombardment and then reacts to form other products. Furthermore, we believe that the H atoms detected probably come from H₂ which is formed directly in the lattice and then escapes. The chemistry is facilitated greatly by being confined in the small spaces of the micropores, or along the track of the penetrating plasma ions. The H atoms will react in the micro-atmosphere in the pores, or be adsorbed on its 'surface' and migrate easily along it. The H atoms on the walls of the pores can more easily find each other and recombine because the activation energy of recombination is reduced for atoms adsorbed on surfaces. They can then desorb as H₂ (Meyer and Pletzer 1986).

Bar-Nun *et al.* (1985) found that H₂ is easily made when they bombarded water ice with Ne⁺ ions to measure sputtered species. As the ice was warmed

from 50 K to 140 K, more H₂ is produced. The H₂ will be made at depth (within the 1st few millimeters) along the track as H atoms become available. Most of what comes off of a bombarded ice at 140 K is H₂, not H. Higher temperatures increase H atom mobility. At lower temperatures (~50 K), H₂O molecules would be the predominant ejecta from sputtering. Bar-Nun *et al.* state that H atoms detected in sputtering experiments originate only from the thin surface monolayers. They found the sputtering yield of H₂ is about 4 times that of H at 140 K. Yield is about 45 molecules/ion for H₂ and 11 molecules/ion for H.

Once at the satellite surface, H₂ will escape, forming part of Ganymede's atmosphere. We suggest that H₂ is manufactured at depth in the solid ice in this way, leaves the satellite as H₂ and then gets dissociated later. H₂ probably co-exists with H in the Ganymede atmosphere.

As for CO, it will be very volatile at typical Galilean satellite temperatures. Its vapor pressure at 70 K (the temperature at the poles) is on the order of 150 millibars (Lide 1996). Once formed from irradiation of CO₂, CO will escape and could form a transitory atmosphere. CO₂ is less volatile than CO; its vapor pressure at 130 K (an equatorial temperature) is ~ 0.31 millibar, so at the equator, the vapor pressure will be low, but still observable.

Migration of volatiles

Lighter gases formed in ices will recondense at night, and also migrate towards the cold traps at the poles. In the Galileo NIMS data from Ganymede (Carlson *et al.* 1996), the 4.25 micron band of CO₂ is predominantly seen in a wide swath around the equatorial region. Water ice is also seen there. CO₂ is much less prominent in the polar regions. This may be because other gases may have sublimated from the equatorial regions and then recondensed on any CO₂ at the poles, keeping them from view, or alternatively, CO₂ is obliterated by the radiation, and processed to other molecules. Water bands are seen at the poles, as well as absorptions from molecules possibly containing -SH and -CN groups, as well as from SO₂ (McCord *et al.* 1997). The sulfur molecules may result from implantation of sulfur ions (Lane *et al.* 1981, Delitsky and Lane 1997). The source of the nitrogen remains an interesting mystery.

The 1.05 μm water ice band is seen in Ganymede's equatorial regions implying that the ice crystals there are larger than at the polar region (Carlson *et al.* 1996). At the poles, the water ice crystals are considered to be more fine-grained and smaller. The 4.25 μm band appears restricted to occurring below 45° N or S latitude, and this maps very well to the connection point of the open magnetic field lines. This implies that the CO₂ band does not appear in

the polar regions because the influx of radiation is so great as to transform most of the CO₂ there to larger organic molecules, such as carbonic acid (H₂CO₃), formaldehyde (H₂CO), and carbon suboxide (C₃O₂), etc. in short timescales.

For CO₂, its crystallization temperature is 65 K. Therefore, it is unlikely there would be any *amorphous* CO₂ on a satellite anywhere because if the CO₂ migrated from the equator to the poles, it would land on 'land' that was at 70 K or greater, that is, ABOVE its amorphous-to-crystalline transition temperature of 65 K. When it reaches the poles, it will deposit as *crystalline* CO₂. Then, it will be subject to the plasma bombardment, and, as Hudson and Moore (1995) showed, when CO₂ is irradiated, amorphous CO₂ does not form, but rather, other products such as CO and C₃O₂. This could explain why the 4.25 μm band is only seen in the equatorial region, and is not detected in the polar regions.

Johnson (1997) noted that the polar caps (bright areas) also start above 40-45° N and S latitude and suggested that this is due to the focusing of radiation along the open field lines which intersect the Ganymede surface above 40° lat. This focusing creates voids and defects in the ice which are more scattering than a solid ice crystal with no defects. This process makes the poles appear bright. This indicates an actual geographic delineation of radiation effects from the unique shape of Ganymede's magnetic field.

If radiation processes CO₂ or H₂O to other molecules, Johnson's explanation for brightening at the poles will still hold if the molecules formed have no absorptions in the visible (which would make the poles darker). This is true for most products of H₂O/CO₂ irradiation. HO₂ has no absorptions above 2600 Å. H₂O₂ has no absorptions above ~ 2800 Å. H₂CO has most of its absorption below 1800 Å with a weak band going only to 3600 Å. Ketene has most of its absorption below 1900, with very weak absorption between 2500 - 4000 Å. HCOOH (formic acid) absorbs below 2600 Å. C₃O₂ absorbs below 3000 Å. CO₂ itself absorbs below 2150 Å, and CO absorbs below 1700 Å (Okabe 1980). Therefore, once these materials are present, voids and defects in them will scatter light in the same way as in pure water ice as long as the optical scattering properties of these species are similar to pure water.

The latitudinal effect on Ganymede is also noted in the emission distribution for oxygen atom airglow at 1356Å seen by Hall *et al* (1998) whose emissions appear to originate in the polar regions. This airglow of O atoms is from that produced by dissociative electron impact of O₂ molecule, which was presumably made in the poles from plasma bombardment of the water ice.

Energy sources and resources

The energy sources available for chemistry at the poles on Ganymede are the copious electrons (0.5 - 3 keV) and low energy magnetospheric particles (< 100 keV) bombarding these regions all the time. Frank *et al.* (1997) measured an electron flux of $\sim 1 \text{ erg/cm}^2 \text{ sec}$ into Ganymede's polar regions. This is equal to $6.0 \times 10^8 \text{ keV/cm}^2 \text{ sec}$. The magnetospheric ion flux at the poles is $2 \times 10^9 \text{ keV/cm}^2 \text{ sec}$ (John Cooper, personal communication, 1998). In the equatorial regions, the surface ices see a magnetospheric ion flux of $5 \times 10^8 \text{ keV/cm}^2 \text{ sec}$ on Ganymede.

Photons contribute $5.0 \times 10^4 \text{ erg/cm}^2 \text{ sec}$, or $3.0 \times 10^{13} \text{ keV/cm}^2 \text{ sec}$ to the surface during daytime. This is calculated from the solar constant of 1373 Watts/m^2 (Jursa 1985), divided by the distance to Jupiter squared, which gives $\sim 56 \text{ W/m}^2$. The actual amount of this energy that can initiate chemistry is that occurring in the UV, below $\sim 2200 \text{ \AA}$. The amount of solar energy that initiates chemistry (bond-breaking, *etc.*) may be $\sim 0.04\%$ of this total of 56 W/m^2 , which is equal to $\sim 1.2 \times 10^{10} \text{ keV/cm}^2 \text{ sec}$. Therefore, UV photons are the largest energy source; however, they are the least penetrating into the ice and only have an effect on the top tens of monolayers. (Monolayers are $\sim 6 - 8 \text{ \AA}$ in width.) Magnetospheric particles and electrons will implant at deeper levels depending on their energy, initiating chemistry there (Cooper, 1997a, 1997b). See Table 1.

Johnson (1990) gives ranges for electron, proton and heavy ion deposition in water ice. Ranges are very similar in both the gas and solid phases, *if expressed in column density*. That is, once the particle traverses the same amount of material, it will be stopped, according to its mass, and velocity. The range is calculated from $R = L/\rho$ where L is column density and ρ is density of the material (Friedlander *et al.* 1964, Delitsky and Thompson 1987). Of course, in the gas phase the range in centimeters will be much longer than in the solid phase.

Ranges for electron traverse in water ice can be up to roughly 750 times as long as the range of ions (O^+ , S^+) in the ice (Johnson 1990). 100 keV electrons will implant typically as far as 0.05 cm into H_2O ice, whereas protons and ions reach down only to $\sim 0.0001 \text{ cm}$. Photons that initiate chemistry (that is, UV photons below $\sim 2200 \text{ \AA}$) only affect the top tens of monolayers ($\sim 100\text{-}300 \text{ \AA}$ range). Therefore, an ice surface will have layers at different depths with somewhat different chemistry, as photons, protons and heavy ions exert individual effects. Chemistry is not only stratified latitudinally, but also vertically. See Figure 5.

In general, if we look at some of the differences in chemical effects with depth, we see that at the very top layer, photolysis will dissociate water into

neutrals, H and OH, or into $O(^3P)$ or $O(^1D)$. Ionization by incoming photons is unlikely because of the low flux of short wavelength solar energy photons able to initiate ionization. Down deeper, where plasma ions deposit ($0.0001 \text{ cm} = 1 \mu\text{m}$), these ions (perhaps an incoming S^+) will act like billiard balls and dissociate H_2O into H and OH along its track, then get neutralized to excited state S^* in the process. When it is about to come to rest, the S^* can then react with an available O from water and create SO (Lane *et al.* 1981) or implant in the interstices and form a bond with the oxygen atom in the water molecule.

Even farther down, electrons can deposit ($0.05 \text{ cm} = 500 \mu\text{m}$). As they traverse the water ice, at first they are going too fast to do much ionization. When they reach a certain reduced velocity, they start to cause more ionization as they go along, and there will be the largest number of ionizations near the end of the track (Johnson 1990). When they finally are slowed almost to their stopping distance, they are then available for electron recombination with charged species such as H_2O^+ . See Figure 5 for a general scheme of these effects with depth.

Electrons and ions will have an energy loss per ion pair formed of $\sim 35 \text{ eV}$. That is, each ion pair in the ice requires 35 eV of energy, and incoming particles will have the energy drained from them as they impact and scatter off of the lattice atoms (Friedlander *et al.* 1964). Incoming particles create a *cylinder of events* as they traverse, causing ionization, dissociation, and formation of excited states, depending on their velocity and energy. If each plasma ion particle is on the order of 100 keV in energy, then it will cause ~ 3000 dissociations before coming to rest in the material. For electrons, their energies are in the range of 0.5 - 3 keV, as reported by Frank *et al.* (1997). If we use a maximum energy of 3 keV, then electrons will cause ~ 100 dissociations before coming to rest. Sputtering is releasing material all the time from the surfaces at the same time, creating a fresh surface for plasma deposition.

In Delitsky and Lane (1997), we calculated an energy flux of ions that was derived from Voyager data reported by Mauk *et al.* (1996). We converted his units of $\text{erg/cm}^2 \text{ sec}^{-1} \text{ sr}$ to $\text{keV/cm}^2 \text{ sec}$ by dividing by 1.6×10^{-9} and multiplying by 2π , because we were assuming a model where we get a hemisphere of radiation rather than a sphere (a reasonable assumption for a satellite without a magnetosphere which experiences radiation only on the trailing side). The Galileo EPD data was converted from directional to omnidirectional flux with π , not 2π , since they assumed isotropic incidence of plasma on a flat surface. Therefore, to compare Voyager versus Galileo data for the energy flux, we use Mauk's data and multiply by π this time. Even with this difference, it appears that the plasma environment of the Jovian magnetosphere near Ganymede has varied in intensity with respect to

location in the ~17 years between the Voyager encounter in 1979 and the first Galileo encounter with Ganymede in 1996 when Galileo EPD spectra were taken (J. Cooper, personal communication, 1998). Variations in Io volcanic activity, which releases some tons of material per second, may affect the temporal ion content of the magnetosphere.

The difference in the energy flux near Ganymede for heavy ions (O^+ , S^+) between Voyager and Galileo time periods is about a factor of 3. See Table 1. The flux was greater during the Voyager time-frame. (Galileo total = 2.5×10^9 versus Voyager = 7×10^9 keV/cm² sec). However, for electrons there is about a 20 fold difference. During Voyager, the electron energy flux near Ganymedes distance was measured as ~ 20 erg/cm² sec (Mauk *et al.* 1996). (This is equal to 1.2×10^{10} keV/cm² sec. See Table 1.) In Frank *et al.* (1997), the electron flux into the poles is reported as ~1 erg/cm² sec (= 6×10^8 keV/cm² sec). The magnetic field intensity of Ganymede is sufficient to be able to deflect all of the electrons into the poles, so this comparison is reasonable. Mauk *et al.* (1996) had noted that the electron flux during Voyager was greater than the heavy ion flux, in terms of energy. During the Galileo era, this is no longer the case. Electron energy flux is now actually less than that of the heavy ions.

Voyager and Galileo data have some other differences as well. Voyager LECP could not distinguish protons from heavy ions, whereas Galileo EPD can. Also, short-time scale differences in particle fluxes (over hours or days) occur, and so the EPD must be time-averaged, which will lead to much lower values. The distance to the plasma sheet is very important, as Europa and Ganymede spend much time in the plasma sheet, whereas at Callisto's distance from Jupiter, the plasma sheet thins out and so the spacecraft approach distance where the measurements were made will have greater impact on the data. The velocities (impacting energies) of the co-rotating plasma of heavy ions increase as the orbital distance increases from Jupiter, but the *volume density* of ions in the plasma sheet decreases rapidly between Europa and Callisto. The amount of time Callisto experiences peak ion concentrations from the plasma sheet will be less than for the other satellites, because the magnetic pole of Jupiter oscillates relative to the orbital plane of the satellites as Jupiter rotates. This causes the plasma sheet to move up and down relative to Callisto's location and change the degree of immersion in the plasma sheet over time.

For Europa, energy flux from Voyager LECP (Mauk *et al.* (1996)) is in good agreement with that of the Galileo EPD (J. Cooper, personal communication, 1998). Therefore, as one goes outward from Europa to Callisto, the differences in measured particle energy fluxes from Voyager to Galileo get larger, because of increasing dependence of the fluxes on distance to the plasma sheet.

Earth-based observations by IUE also have noted differences in hemispheric asymmetries over this 17-year period. Domingue and Lane (1998) detected a time variable absorbance from the SO₂ frost on Ganymede's trailing hemisphere, implying that the decrease in particle flux to the satellite (yielding less S⁺ implantation, and so less SO₂ formation) may be responsible for this change.

Special case of Ganymede

If we take Ganymede as a special case because of its unique magnetic field which redirects the plasma ions, then we can consider 2 patches of ice on Ganymede as endmembers of a set of patches at different latitudes. Patch A is a square centimeter of ice at the poles, and Patch B is a square centimeter of ice at the equator. Table 1 sums up their energy inputs. From Galileo plasma data, it is determined that the plasma ion energy deposition into the poles is ~ 4 times that into the equatorial region ($E_{\text{poles}} = 2 \times 10^9$; $E_{\text{eq}} = 5 \times 10^8$ keV/cm² sec). The global energy deposition as measured by Voyager is also included.

Patch A stays at 70-80 K all of the time. It is bombarded by electrons and plasma ions, and sees no photons. Long-chain molecules, once formed, will persist and lengthen. The cold temperatures and lack of mobilities of products will eventually lead to polymerization (as in the case of formaldehyde or C₃O₂). This might explain why no CO₂ is seen (it's all used up). Mobilities are slow, but this patch has billions of years for radicals to move around and react. Radical addition reactions require almost no activation energy so the process can proceed more easily than may be expected in the cold temperatures.

Patch B at the equator will have a somewhat different chemical scenario, in that smaller molecules formed (like CO, H₂ etc.) may escape from the diurnal heating before much long-chain chemistry may occur. The chemistry is different because some of the reactants are leaving (and volatilizing). However, increased mobility of radicals such as HCO, HO₂ and OH will facilitate the formation of some large molecules, probably different ones than those that require light molecules like H, CO, H₂ which are escaping while the surface is being heated during daylight hours.

Table 2 shows some of the chemical pathways that may result from these processes. Water fragmentation products are shown as well as theoretical wavelength limits for dissociation of reactant molecules.

Table 3 gives column densities of molecules produced on Ganymede over 1000 years for the equator and polar regions. They are calculated using the equation $N = EGt$ (Delitsky and Thompson 1987) where N is column density (molecules/cm²), E is energy flux (keV/cm² sec), G is the radiation

yield in units of molecules/100 eV of energy deposited, and t is time. G values are used from Johnson (1990), DelloRusso *et al.* (1993) and Delitsky and Lane (1997) and are for yields of products from H_2O/CO_2 experiments. Some G values used in Table 3 are actually from radiolysis experiments of secondary products with water (such as H_2CO/H_2O), and since the H_2CO must first be made from the H_2O/CO_2 reaction, the actual G value direct from H_2O/CO_2 radiolysis may be lower. G values depend on initial concentrations, therefore, the column densities for products calculated in these few cases would be upper limits.

In closing, we will point out that this type of regional effect on chemistry in the surfaces will also apply to the icy satellites of Saturn, Uranus and Neptune. Magnetospheric particle fluxes may have complex topologies because of magnetic pole tilts of the planets that are at large angles to the rotation axes. This will create unusual energy depositions onto the satellites. They also are likely to have more amorphous phases of their volatiles, such as water and CO_2 , due to the lower temperatures there (< 85 K for Saturnian satellites). Given the complex nature of the magnetospheres of Uranus and Neptune, the effect of their shapes on surface chemistry of the satellites may be a challenge to fully characterize.

Summary

1. Complex molecules from H_2O/CO_2 radiolysis on the satellite surfaces resulting from magnetospheric plasma ion bombardment may occur on Europa, Ganymede and Callisto. Based on laboratory studies, possible molecules that may result are: CH_3OH , H_2CO , CH_2CO , C_3O_2 , $HCOOH$, CO , CH_3COOH , H_2CO_3 , $HCOOCH_3$, $(CH_3)_2CO$, CH_3CH_2OH , $HOCH_2CH_2OH$, polymeric C_3O_2 and polymeric H_2CO (POM). The water fragmentation products OH , O_2 , HO_2 , H_2O_2 , and O_3 will also occur. These may be observable in ground-based spectra, as many of these molecules have easily discernable active infra-red bands.

2. Ganymede's unique magnetic field shape will lead to different regional chemical scenarios than would otherwise result from the standard model of magnetospheric plasma deposition effects only occurring on the trailing side (as for Europa and Callisto). Greater energy deposition occurs in Ganymede's polar regions than in the equatorial regions, due to the focusing of magnetospheric plasma radiation along its open field lines. The ratio of plasma energies into the poles to those into the equator is ~ 4 .

3. The polar caps on Ganymede will have increased void production from this particle focusing, as recognized by Johnson (1997), but most molecules formed in our H_2O/CO_2 scenarios have no absorptions in the visible, and so any defects and voids created by the radiation will scatter light as they do in

water ice. Detection of oxygen atom airglow emanating from higher latitudes by Hall *et al.* (1998) further supports a model of chemical processing happening preferentially in the polar regions.

4. The lack of leading/trailing asymmetry on Ganymede of the 2800 Å band in the UV spectrum is consistent with our understanding of the plasma redistribution flowing mainly to the poles due to the effect of the magnetic field. The leading/trailing asymmetry seen in the 2800 Å band on Europa (Lane *et al.* 1981) correlates well with the weakness of the magnetic field of this satellite. The asymmetry on Callisto is also consistent with its lack of any significant magnetic field (Domingue and Lane 1997).

5. The H atmosphere seen around Ganymede probably co-exists with H₂ in the Ganymede atmosphere, as hydrogen is more readily formed as H₂ rather than H in a plasma bombarded water ice.

6. CO is easily formed from CO₂ radiolysis. CO and CO₂ would have fairly high vapor pressures in the temperature ranges occurring on the Galilean satellites. We predict that if CO₂ is indeed the identification of the 4.25 μm band in NIMS spectra, then the presence of CO may be observable in an atmosphere on these satellites with high-resolution instruments.

Acknowledgments: We would like to thank John Cooper for his excellent and very helpful descriptions of the plasma energies near the satellites from Galileo data. We also thank Reggie Hudson, Marla Moore, Bob Johnson and Tom Tidwell for information about chemistry and energy inputs. We also acknowledge Lew Chadderton, Margaret Kivelson and Steven Squyres, as well as Academic Press and Nature (London) for their kind permission to reprint figures from their publications. The research described in this paper was carried out by the Jet Propulsion Laboratory/California Institute of Technology under contract with the National Aeronautics and Space Administration.

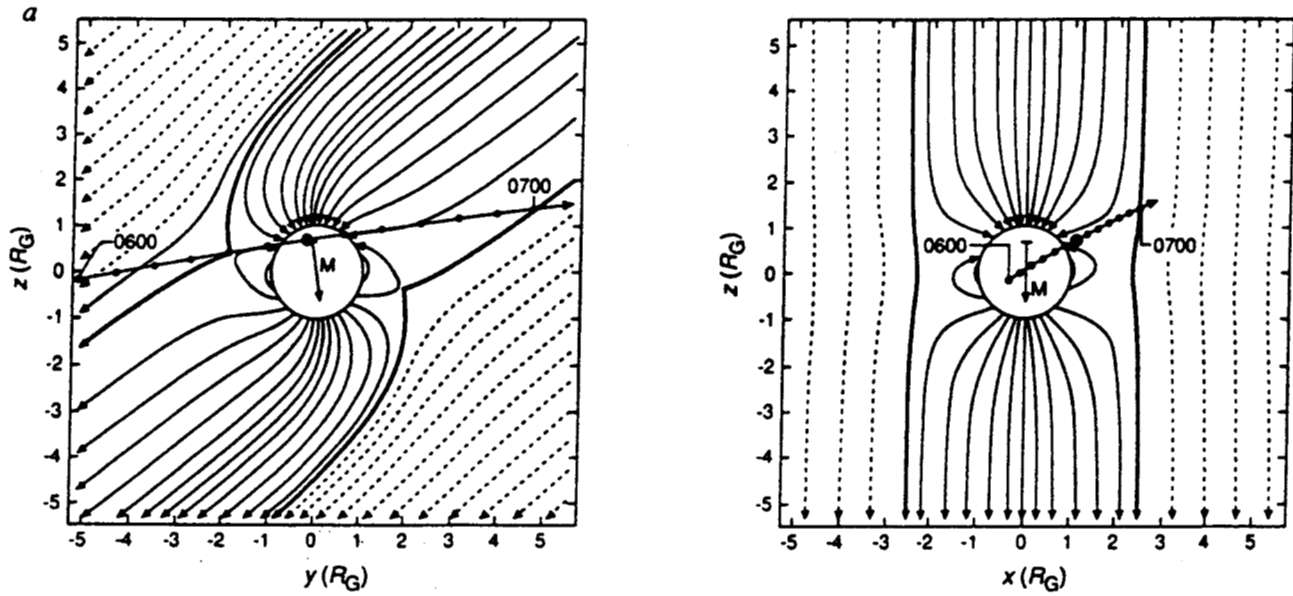


Figure 1: Shape of Ganymede's magnetic field seen from 2 directions
 a) along its orbit (y direction is towards Jupiter) b) looking towards Jupiter
 (x direction is along Ganymede's orbit) The path of Galileo is shown in bold.
 From *Kivelson et al. 1996*

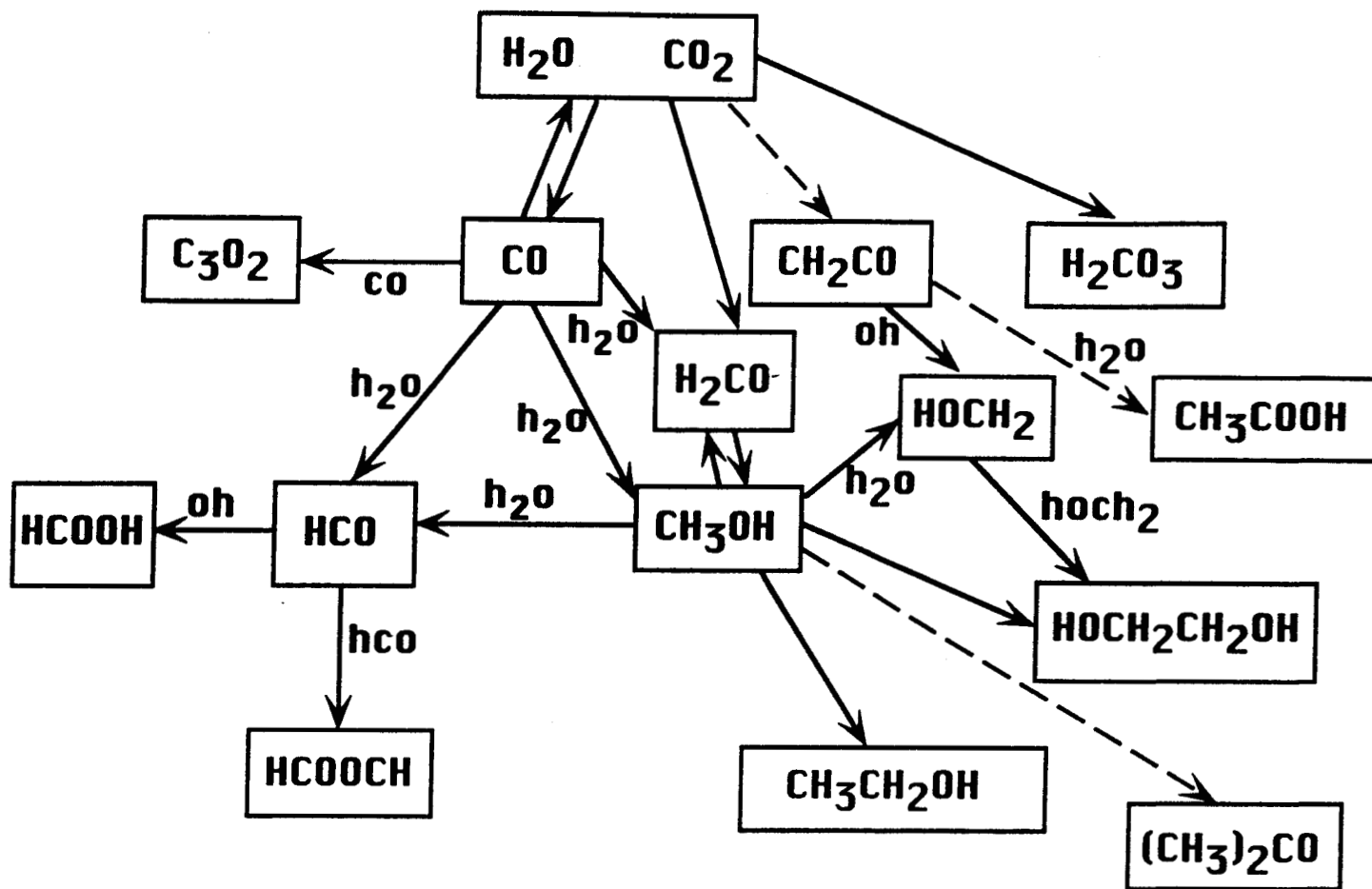


Figure 2: Reaction pathways that occur in irradiated $\text{H}_2\text{O}/\text{CO}_2$ ices, derived from laboratory experiments. Products from $\text{H}_2\text{O}/\text{CO}_2$, such as CO , when irradiated in the presence of the abundant H_2O , then yield larger molecules. For example, $\text{CO} + \text{H}_2\text{O} + \text{irradiation} \rightarrow \text{CH}_3\text{OH}$. Not all pathways are shown. Dotted lines are pathways for products that need additional lab confirmation. This figure is meant to illustrate the variety of CHO-containing molecules that may occur on the satellites.

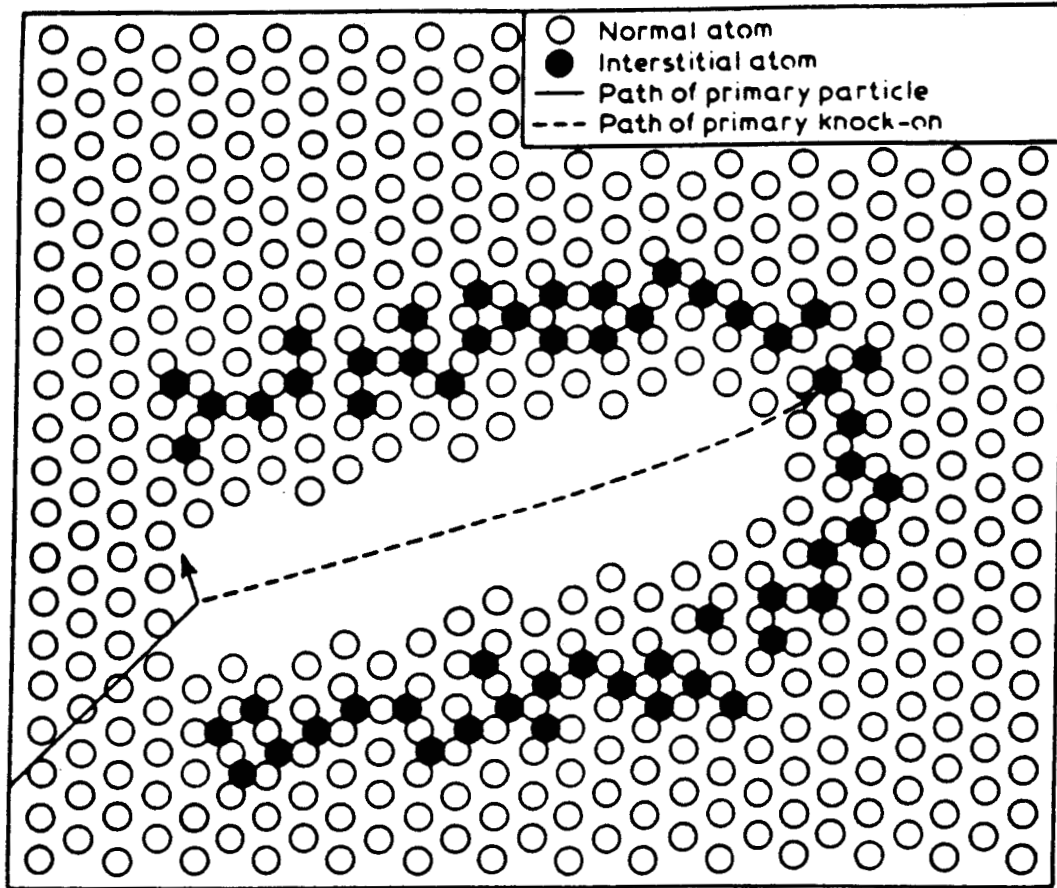


Figure 3: Representation of defect creation in ice, showing interstitial atoms around a multiple vacancy during production of a Brinkman displacement spike. From *Chadderton and Torrens 1969*

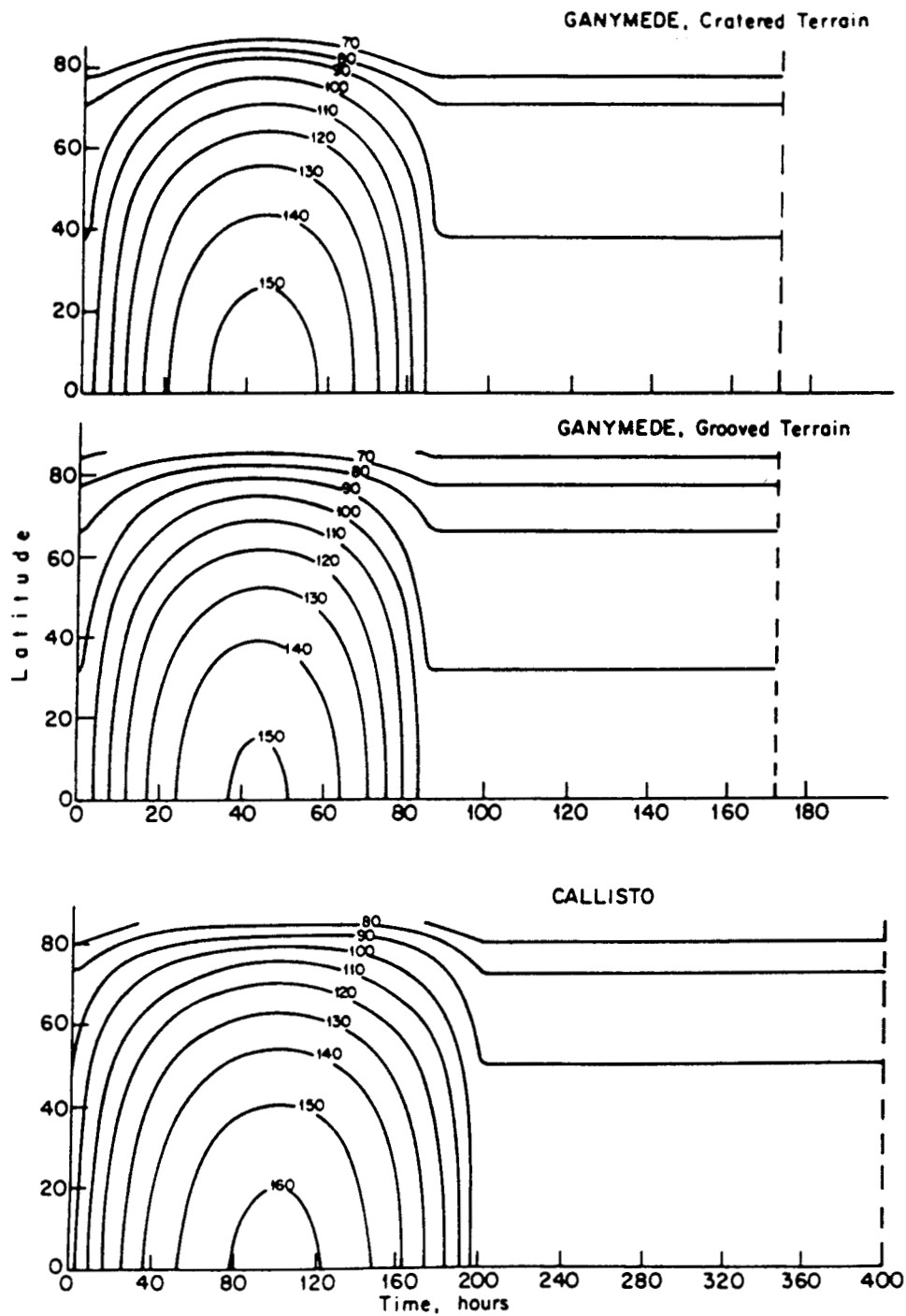


Figure 4: Surface temperatures for Ganymede and Callisto, showing variations over a satellite day with latitude. Europa's contours are similar but only reach 120 K on the day side. From *Squyres 1980*.

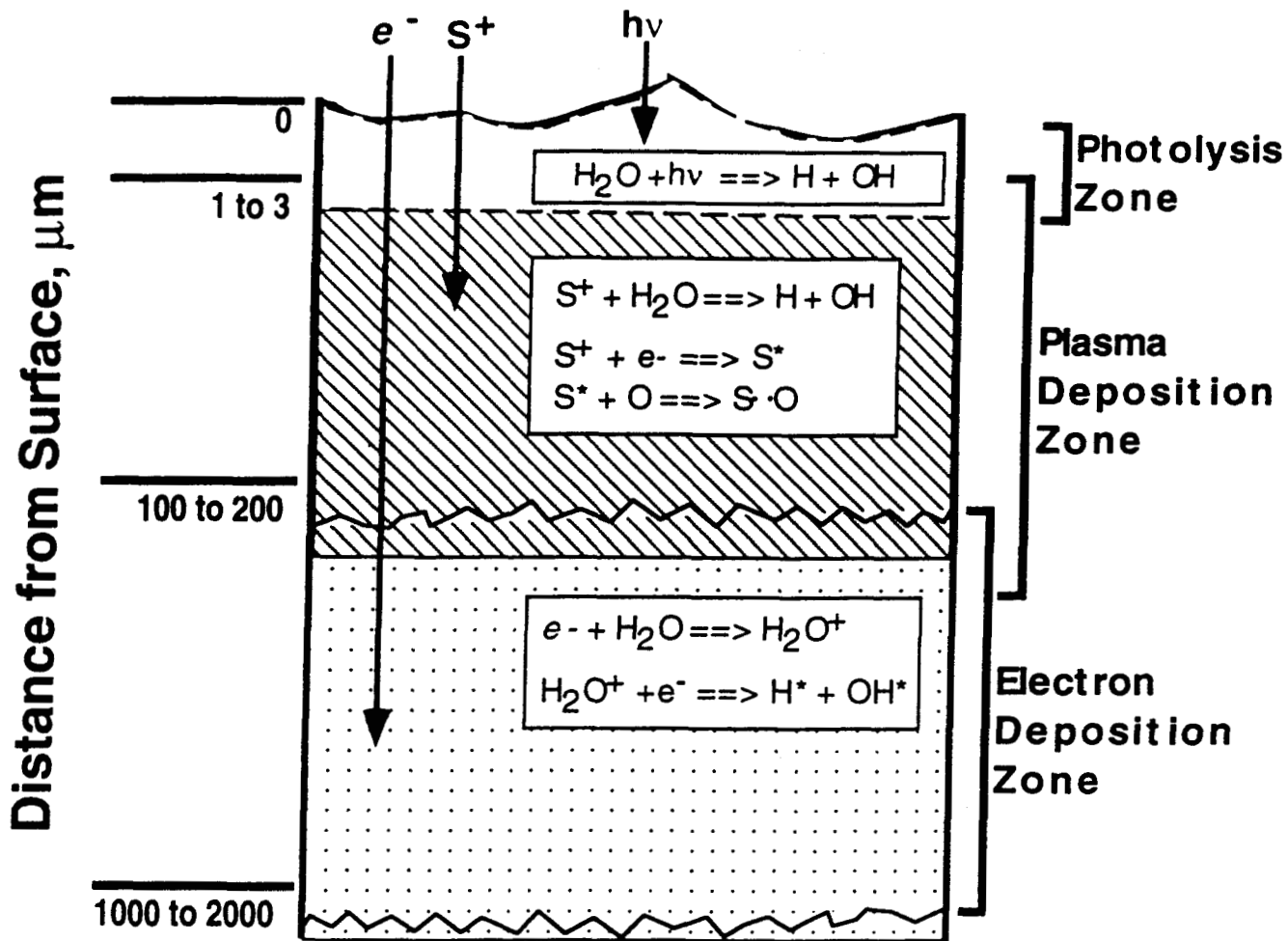


Figure 5: Schematic of irradiation effects with depth to show some of the differences from the nature of the incoming radiation. UV and visible photons dissociate top layer molecules to neutrals. Plasma ions (such as S^+) act like billiard balls dissociating molecules, then get neutralized by stationary electrons or change exchange to an excited state, which can react with, for example, O to form S - O bonds. (Stationary electrons are shown as e^-). Electron impact from magnetospheric electrons will mostly ionize molecules along their track (Incoming fast electrons are indicated by e^- (italic)). When they finally come to rest, they can dissociatively recombine with ionized molecules, creating excited state neutrals like O^* or OH^* .

Table 1: Energy Inputs to Ganymede (units of keV/cm² sec)

<u>Patch</u>	<u>Location</u>	<u>Plasma ions</u>	<u>Electrons</u>	<u>Photons</u>	<u>Thermal</u>
A	Polar	2×10^9	6×10^8	~ 0	no heating ; ice amorphous
B	Equatorial	5×10^8	~ 0	1.3×10^{10}	heated to 150 K every 170 hours
	Voyager	7×10^9	1.2×10^{10}	1.3×10^{10}	

Table 2: Reactions possible in a H₂O/CO₂ ice on a Galilean satellite surface
 (p refers to particle (ion, electron) bombardment; M refers to a third body (or wall of void in ice) to absorb excess energy of reaction.)

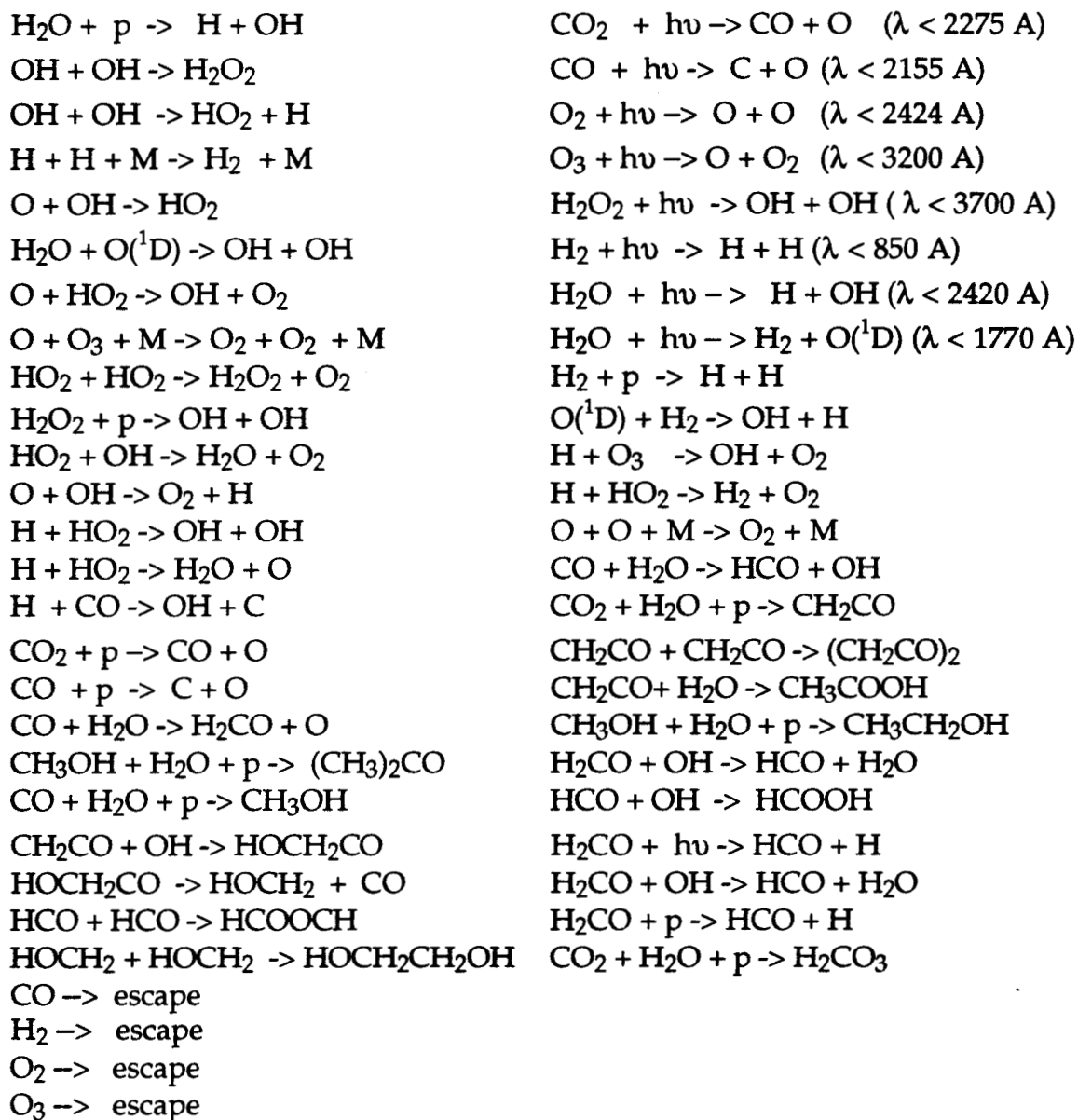


Table 2a: Name table

H ₂ CO	formaldehyde	CH ₃ OH	methanol
HCOOH	formic acid	H ₂ CO ₃	carbonic acid
CH ₂ CO	ketene	HCOOCH	glyoxal
CH ₃ COOH	acetic acid	HOCH ₂ CH ₂ OH	ethylene glycol
CH ₃ CH ₂ OH	ethanol		

Table 3

Column densities of materials calculated from $N=EGt$, where

$t = 1000$ years, for poles and equator of Ganymede

For a H_2O/CO_2 surface, using Galileo plasma energy measurements

(N =molecules/cm²; L =g/cm²)

Species	G	N_{poles}	L_{poles}	N_{equat}	L_{equat}
H_2O_2	0.4	3.2×10^{20}	0.0181	6.2×10^{19}	0.0035
HO_2	0.4	3.2×10^{20}	0.0178	6.2×10^{19}	0.0034
OH	0.3	2.5×10^{20}	0.0069	4.7×10^{19}	0.0013
O_2	0.15	1.2×10^{20}	0.0065	2.3×10^{19}	0.0012
H_2	0.7	5.7×10^{20}	0.0019	1.1×10^{20}	0.0003
H_2CO_3	0.5	4.0×10^{20}	0.0416	7.7×10^{19}	0.0079
H_2CO	1.0	8.2×10^{20}	0.0403	1.6×10^{20}	0.0079
CH_2CO	(0.5)	4.0×10^{20}	0.0270	7.7×10^{19}	0.0053
HCO	(0.05)	4.0×10^{19}	0.0019	7.7×10^{18}	0.00037
C_3O_2	(0.5)	4.0×10^{20}	0.0455	7.7×10^{19}	0.0087
CH_3OH	0.04*	3.2×10^{19}	0.0017	6.2×10^{18}	0.00033
CH_3COOH	(0.1)	8.2×10^{19}	0.0081	1.6×10^{19}	0.0016
$(CH_3)_2CO$	(0.5@)	4.0×10^{20}	0.0385	7.7×10^{19}	0.0074
HCOOH	0.3*	2.5×10^{20}	0.0191	4.7×10^{19}	0.0036
HCOOCH	(0.1#)	8.2×10^{19}	0.0079	1.6×10^{19}	0.0015
$(HOCH_2)_2$	(0.1)	8.2×10^{19}	0.0084	1.6×10^{19}	0.0016
CH_3CH_2OH	(0.01)	8.2×10^{18}	0.00062	1.6×10^{18}	0.00012

* from CO/H_2O expts

from H_2CO/H_2O expts

@ from CH_3OH/H_2O expts

Notes: G values are in units of molecules/100 eV. G values used here for all species are for the radiolysis yield of that species from H₂O/CO₂ mixtures except where noted. G values are from Delitsky and Lane (1997), DelloRusso et al 1993, Johnson (1990) and M. Moore, personal communication, 1998. Calculation for poles of Ganymede uses total of magnetospheric plasma and electron deposition as an energy source (= 2.6x10⁹ keV/cm²sec). Calculation for equator uses only magnetospheric particle deposition as an energy source (= 5.0x10⁸ keV/cm²sec). Photons are excluded for this calculation as they do not operate at depth. Therefore, the values for the equatorial region are minimums. G values in parentheses are estimates.

REFERENCES

- Allen, A.D., M.A. McAllister, and T.T. Tidwell, Kinetic and theoretical studies of the hydration of carbon suboxide, *J. Chem., Soc. Chem. Commun.*, **24**, 2547 (1995)
- Anderson, A.R., J.V.F. Best and M.J. Willett, Proton radiolysis of carbon monoxide, *Trans. Faraday Soc.* **62**, 595 (1966)
- Baratta, G.A., A.C. Castorina, G. Leto, M.E. Palumbo, F. Spinella and G. Strazzulla, Ion irradiation experiments relevant to the physics of comets, *Planet. Space. Sci.*, **42**, 759 (1994)
- Bar-Nun, A., G. Herman, M.L. Rappaport and Y. Mekler, Ejection of H₂O, O₂, H₂ and H from water ice by 0.5-6 keV H⁺ and Ne⁺ ion bombardment, *Surf. Sci.*, **150**, 143 (1985)
- Barth, C.A., C.W. Hord, A.I.F. Stewart, W.R. Pryor, K.E. Simmons, W.E. McClintock, J.M. Ajello, K.L. Naviaux, and J.J. Aiello, Galileo ultraviolet spectrometer observations of atomic hydrogen in the atmosphere of Ganymede, *Geophys. Res. Lett.*, **24**, 2147 (1997)
- Benit. J., Bibring J. P. and Rocard, F. , Chemical irradiation effects in ices, *Nucl. Inst. Meth.*, **B32**, 349(1988)
- Bothe, E., A.M. Dessouki and D. Schulte-Frohlinde, Rate and mechanism of the ketene hydrolysis in aqueous solution, *J. Phys. Chem.*, **84**, 3270 (1980)
- Briggs, J.P. and P.G. Clay, Formation of polymeric carbon suboxide during gamma radiolysis of liquid carbon monoxide at 77 K, *Nature*, **218**, 355 (1968)
- Brucato, J.R., A.C. Castorini, M.E. Palumbo, M.A. Satorre and G. Strazzulla, Ion irradiation and extended CO emission in cometary comae, *Planet. Space Sci.*, **45**, 835 (1997a)

Brucato, J.R., M.E. Palumbo and G. Strazzulla, Carbonic acid by ion implantation in water/carbon dioxide ice mixtures, *Icarus*, **125**, 135 (1997b)

Calvin W.M., Clark R. N., Brown R.H., and Spencer J.R., Spectra of the icy galilean satellites from 0.2 to 5 μ - a compilation, new observations, and a recent summary, *J.Geophys. Res.*, **100**, 19041(1995)

Calvin W.M. , Johnson R. E., Spencer J. R. , O₂ on Ganymede - spectral characteristics and plasma formation mechanisms, *Geophys. Res. Lett.* **23**, 673 (1996)

Calvin, W.M. and Spencer, J.R., Latitudinal distribution of O₂ on Ganymede: observations with the Hubble Space Telescope, *Icarus*, **130**, 505 (1997)

Carlson R.W., et al., Near-infrared spectroscopy and spectral mapping of Jupiter and the Galilean satellites: Results from Galileo's initial orbit, *Science*, **274**, 385 (1996),

Chadderton, L.T. and I. M. Torrens, *Fission Damage in Crystals*, Methuen (London), 1969, ch. 2

Cooper, J. F., N. Gehrels, R. E. Johnson, C. M. Cohen, and N. Murphy, Energetic ion irradiation of the Galilean satellites, *EOS, Transactions, Amer. Geophys. U.*, 1997 Spring Meeting Suppl., **78**(17), S307, 1997.

Cooper, J. F., B. H. Mauk, C. M. Cohen, R. E. Johnson, and N. Gehrels, Irradiation of icy galilean satellites by energetic ions: calculations derived from Galileo EPD and HIC flux spectra, *EOS, Transactions, Amer. Geophys. U.*, 1997 Fall Meeting Suppl., **78**(46), F418, 1997.

Delitsky, M.L., Report on Cometary Chemistry, University of Michigan Space Physics Research Laboratory report, 1980

Delitsky, M.L. and A.L. Lane, Chemical schemes for surface modification of icy satellites: A road map, *J. Geophys.Res.* , **102**, 16385 (1997)

Delitsky, M.L. and W.R. Thompson, Chemical processes in Triton's atmosphere and surface, *Icarus*, **70**, 354 (1987)

DelloRusso, N., R.K. Khanna and M.H. Moore, Identification and yield of carbonic acid and formaldehyde in irradiated ices, *J. Geophys. Res.*, **98**, 5505 (1993)

Devlin, J.P. and V. Buch, Vibrational spectroscopy and modeling of the surface and subsurface of ice and of ice-adsorbate interactions, *J. Phys. Chem. B*, **101**, 6095 (1997)

Dessler, A.J., *Physics of the Jovian Magnetosphere*, Cambridge University Press, 1983

Domingue, D.L. and A. L. Lane, Secular ultraviolet studies of the Galilean satellites, 'Ultraviolet astrophysics, Beyond the IUE final archive', conference proceedings, Nov 1997, Sevilla, Spain, ESA SP-413, Feb 1998

Frank L.A., W.R. Paterson, K.L. Ackerson and S.J. Bolton, Low-energy electron measurements at Ganymede with the Galileo spacecraft: probes of the magnetic topology, *Geophys. Res. Lett.* **24**, 2159 (1997)

Friedlander, G., J.W. Kennedy and J.M. Miller, *Nuclear and Radiochemistry*, Wiley, New York, 1964

Geiss, J. et al., Plasma composition in Jupiter's magnetosphere: Initial results from the solar wind ion composition spectrometer, *Science*, **257**, 1535 (1992)

Gerakines, P.A., W.A. Schutte and P. Ehrenfreund, Ultraviolet processing of interstellar analogs, I. pure ices, *Astron. Astrop.* **312**, 289 (1996)

Hage, W., K.R. Liedl, A. Hallbrucker and E. Mayer, Carbonic acid in the gas phase and its astrophysical relevance, *Science*, **279**, 1332 (1998)

Hagen, W., A.G.G.M. Tielens and J.M. Greenberg, A laboratory study of the infrared spectra of interstellar ices, *Astron. Astrop. Supp. Ser.* **51**, 389 (1983)

Hall, D.T., P.D. Feldman, M.A. McGrath and D.F. Strobel, The Far-ultraviolet oxygen airglow of Europa and Ganymede, *Astrop. J.*, **499**, 475 (1998)

Hallamasek, D., E. Babka, and E. Knozinger, How inert is an argon matrix?, *J. Molec. Struct.*, **408/409**, 125 (1997)

Hobbs, P.V, *Ice physics* , 837 pp., Clarendon Press, Oxford, 1974

Hudson, R.L. and B. Donn, An experimental-study of the sublimation of water ice and the release of trapped gases, *Icarus*, **94**, 326 (1991)

Hudson R.L. and M.H. Moore, Far-IR spectral changes accompanying proton irradiation of solids of astrochemical interest, *Radiat. Phys. Chem*, **45**, 779 (1995)

Jursa, A. S., ed., *Handbook of Geophysics and the Space Environment*, Air Force Geophysics Laboratory, 1985

Johnson, R.E., *Energetic Charged-Particle Interactions with Atmospheres and Surfaces*, 232 pp., Springer, New York, 1990

Johnson, R.E., Polar 'caps' on Ganymede and Io revisited, *Icarus*, **128**, 469 (1997)

Johnson, R.E. and T.I. Quickenden, Photolysis and radiolysis of water ice on outer solar system bodies, *J. Geophys. Res.*, **102**, 10985 (1997)

Khurana, K.K., Kivelson M. G., Russell C.T., Walker R. J., and Southwood D. J., Absence of an internal magnetic-field at Callisto, *Nature* **387** 262 (1997)

Kivelson, M.G., K.K. Khurana, C.T. Russell, R.J. Walker, J.Warnecke, F.V. Coroniti, C. Polanskey, D.J. Southwood, and G. Schubert, Discovery of Ganymede's magnetic field by the Galileo spacecraft, *Nature*, **384**, 537 (1996)

Kivelson, M.G., K.K. Khurana, F.V. Coroniti, S. Joy, C.T. Russell, R.J. Walker, J. Warnecke, L. Bennett and C. Polanskey, The magnetic field and magnetosphere of Ganymede, *Geophys. Res. Lett.*, **17**, 2155 (1997a)

Kivelson, M.G., K.K. Khurana, S. Joy, C.T. Russell, D.J. Southwood, R.J. Walker, and C. Polanskey, Europa's magnetic signature: report from Galileo's pass on 19 December 1996, *Science*, **276**, 1239 (1997b)

Kouchi, A. and T. Kuroda, Amorphization of cubic ice by ultraviolet irradiation, *Nature*, **344**, 134 (1990)

Lane, A.L., R.M. Nelson and D.L. Matson, Evidence for sulphur implantation in Europa's UV absorption band, *Nature*, **292**, 38 (1981)

Leto, G., M.E. Palumbo and G. Strazzulla, Structural characteristics of irradiated and unirradiated ices, *Nucl. Inst and Meth.* **B116**, 49 (1996)

Lide, D.R. ed., *CRC Handbook of Chemistry and Physics*, CRC Press, New York, 1996

Mauk B.H., Gary S.A., Kane M., Keath, E.P. Krimigis, S.M., and Armstrong T.P., Hot plasma parameters of Jupiter's inner magnetosphere, *J. Geophys. Res.*, **101**, 7685 (1996)

McCord, T.B. et al., Organics and other molecules in the surfaces of Callisto and Ganymede, *Science* **278**, 271 (1997)

Meyer, E. and R. Pletzer, Astrophysical implications of amorphous ice - a microporous solid, *Nature*, **319**, 298 (1986)

Moore, M.H., R.F. Ferrante and J.A. Nuth, Infrared spectra of proton irradiated ices containing methanol, *Planet. Space Sci.* **44**, 927 (1996)

Moore, M.H. and R.K. Khanna, Infrared and mass-spectral studies of proton irradiated H₂O + CO₂ ice: evidence for carbonic acid, *Spectrochimica Acta* **47**, 255 (1991)

Moore, M.H., R.K. Khanna, and B. Donn, Studies of proton irradiated H₂O + CO₂ and H₂O + CO ices and analysis of synthesized molecules, *J. Geophys. Res.*, **96**, 17541 (1991)

Okabe, H. *Photochemistry of small molecules*, 431 pp., John Wiley, New York, 1978

Orton, G.S., J.R. Spencer, L.D. Travis, T.Z. Martin, and L.K. Tamppari, Galileo photopolarimeter-radiometer observations of Jupiter and the Galilean satellites, *Science*, **274**, 389 (1996)

Palumbo, M.E. and G. Strazzulla, The 2140 cm⁻¹ band of frozen CO: laboratory experiments and astrophysical applications, *Astron. Astrophys.* **269**, 568 (1993)

Pincock, R. E., Reactions in frozen systems, *Acc. Chem. Res.*, **2**, 97 (1969)

Ratcliffe, C.I. and J.A. Ripmeester, ¹H and ¹³C NMR studies on carbon dioxide hydrate, *J. Phys. Chem.*, **90**, 1259 (1986)

Sandford, S.A., L.J. Allamandola, A.G.G.M. Tielens and G.J. Valero, Laboratory studies of the infrared spectral properties of CO in astrophysical ices, *Astrop. J.* **329**, 498 (1988)

Schmitt, B., R. Grim and J.M. Greenberg, Spectroscopy and Physico-chemistry of CO:H₂O and CO₂:H₂O ices, ESA SP-290, p. 213, (1989), (Proc. 22nd Eslab Symp on IR spectroscopy in Astronomy, Salamanca, Spain, Dec 1988)

Schutte, W.A. , P.A. Gerakines, T.R. Geballe, E.F. van Dishoeck and J.M. Greenberg, Discovery of solid formaldehyde toward the protostar GL 2136: observations and laboratory simulation, *Astron. Astrop.* **309**, 633 (1996)

Siegel, S., J.M. Flournoy and L.H. Baum, Irradiation yields of radicals in gamma-irradiated ice at 4.2 and 77 K, *J. Chem. Phys.*, **34**, 1782 (1961)

Smith, R.N., D.A. Young, E.N. Smith and C.C. Carter, The structure and properties of carbon suboxide polymer, *Inorg. Chem.*, **2**, 829 (1963)

Smoluchowski, R. and A. McWilliam, Structure of ices on satellites, *Icarus*, **58**, 282 (1984)

Squyres, S.W., Surface temperatures and retention of H₂O frost on Ganymede and Callisto, *Icarus*, **44**, 502 (1980)

Strazzulla, G., A.C. Castorini and M.E. Palumbo, Ion irradiation of astrophysical ices, *Planet. Space Sci.*, **43**, 1247 (1995a)

Strazzulla, G., M. Arena, G.A. Baratta, A. Castorini, G. Celi, G. Leto, M.E. Palumbo and F. Spinella, Radiation chemistry of ices of planetological interest at low temperature, *Adv. Space Res.*, **16** (#2), 61 (1995b)

Strazzulla, G., G.A. Baratta, G. Leto and G. Foti, Ion-Beam-Induced amorphization of crystalline water ice, *Europhysics Letters*, **18**, 517(1992)

Sugimoto, S., M. Nishii and T. Sugiura, Radiation-induced chemical reactions of carbon-monoxide and hydrogen mixture 3. Solid materials produced under irradiation, *Radiat. Phys. Chem.*, **27**, 147 (1986)

Tidwell, T.T., unpublished manuscript, 1997

Unwin, P.N.T. and J. Muguruma, Electron microscope observations of the defect structure of ice, *Phys. Stat. Sol.*, **14**, 207 (1972)

Urquhart, M.L. and B. M. Jakosky, Constraints on the solid-state greenhouse on the icy Galilean satellites, *J. Geophys. Res.*, **101**, 21169 (1996)

Whipple, F., 'Comets', in *Cosmic Dust*, Chichester, 1978

Williams, D. J., B. H. Mauk, R.W. McEntire, E. C. Roelof, T. P. Armstrong, B. Wilken, J.G. Roederer, S.M. Krimigis, T.A. Fritz, L.J. Lanzerotti, and N.

Murphy, Energetic particle signatures at Ganymede; implications for Ganymede's magnetic field, *Geophys. Res. Lett.*, **24**, 2163 (1997)