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The destruction and growth of dust grains in interstellar space – II. Destruction by grain surface reactions, grain–grain collisions and photodesorption

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Summary. Chemical reactions on the surfaces of ice grains are shown to be unimportant as destruction agents. However, graphite grains can be destroyed by reaction with chemisorbed hydrogen and oxygen atoms, for grain temperatures in excess of ~ 65 K, leading to an explanation for the weakness of the 2175 Å extinction feature towards several stars embedded in H II regions. It is also shown that such reactions govern the conditions under which graphite grains can condense in stellar atmospheres. The classical Oort–van de Hulst destruction mechanism of grain–grain collisions during cloud collisions is shown to be ineffective, by means of a detailed consideration of the shock wave structure at the interface between the colliding clouds. Magnetic field influenced grain collisions in shock fronts, between grains from the same cloud, do not lead to a significant overall destruction rate for dust grains in the interstellar medium. It is argued that photodesorption is the dominant destruction mechanism for ice grains held together by weak van der Waals dispersion forces. The timescale for destruction of an ice grain of radius 10^{-5} cm by the interstellar ultraviolet radiation field is derived to be ~ 5×10^4 yr, much shorter than for other destruction mechanisms.

1 Grain surface reactions

1.1 CHEMICAL SPUTTERING OF ICE GRAINS

Wickramasinghe & Williams (1968) have suggested that the reaction

$$H_2O + H \rightarrow OH + H_2 \qquad \text{(a)}$$

could act as a significant destruction mechanism for ice grains in regions where H atoms have sufficient energy to overcome the endothermicity and activation energy of the reaction. The reaction is endothermic by ~ 0.64 eV (the difference in the dissociation energies of H_2O and H_2) and Wickramasinghe & Williams calculated an activation energy of 0.28 eV, giving a

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temperature dependence for the reaction proportional to $\exp(-0.92/kT) = \exp(-10\,650/T)$, where T is the temperature of H_2O and H in the gas phase. Mayer, Schieler & Johnston (1967) have found experimentally that the reaction rate is proportional to $\exp(-9400/T)$, in good agreement with the estimate of Wickramasinghe & Williams. However, Wickramasinghe & Williams assumed that the probability of reaction between an impinging H atom and an H_2O lattice molecule was given by the exponential term alone, whereas the reaction is in competition with normal kinetic (elastic) collisions. The full reaction rate determined by Mayer *et al.* (1967) was $4.3 \times 10^{-13} T^{0.68} \exp(-9400/T)\,\mathrm{cm^3/s}$, which according to standard reaction kinetics theory is the product of a reaction cross section σ_R, a mean thermal velocity and an exponential term giving the fraction of particles with energy greater than the reaction energy E'. Therefore

$$4.3 \times 10^{-13} T^{0.68} \exp(-9400/T) = \sigma_R \left(\frac{8kT}{\pi\mu'}\right)^{1/2} \exp(-E'/kT)$$

where μ' is the reduced mass of the H_2O–H system $[\mu = m_H m_{H_2O}/(m_H + m_{H_2O}) = 0.947 m_H]$. Taking the term $T^{0.68}$ to be equal to $T^{1/2}$ within the experimental errors, we find $\sigma_R = 2.9 \times 10^{-17}\,\mathrm{cm^2}$. The cross section for normal kinetic (hard-sphere) collisions is equal to $10^{-15}\,\mathrm{cm^2}$ (this is also equal to the mean area per surface molecule on a grain surface), so that the probability of a reaction per incident H atom, called here the chemical sputtering yield, Y_{ch}, is given by

$$Y_{ch} = 2.9 \times 10^{-2} \exp(-9400/T).$$

We note that even if there is a reaction there is no guarantee that the OH radical will leave the surface, so that Y_{ch} is an upper limit.

We now consider the possible importance of chemical sputtering for ice grains in shock waves. For a shock velocity of $v_M = 10$ km/s we derive an equivalent mean H atom temperature of $T = 4 \times 10^3$ K, which gives $Y_{ch} = 2.8 \times 10^{-3}$. We find, for a grain lifetime given by

$$\tau_{ch} = 4a\rho_g / n_H v_M Y_{ch} m_{H_2O}$$

that for $n = 40\,\mathrm{cm^{-3}}$, $\tau_{ch} = 4.1 \times 10^5$ yr; longer than the lifetime against physical sputtering for ice grains with sublimation energy $H_s = 0.1$ eV, and very much longer than the grain slowing time and gas cooling time, which are $< 10^4$ yr. Thus chemical sputtering of ice grains will be of no importance in the interstellar medium.

1.2 GRAPHITE GRAIN SURFACE REACTIONS

The type of surface chemical reaction considered in the previous section is essentially a modification of a gas kinetic reaction and could only occur during the impact of an impinging atom on a lattice molecule. If an impinging atom should be trapped and stick to the surface of an ice grain it would subsequently never have sufficient energy to overcome the large potential barrier to reaction (a). An entirely different type of surface reaction, and one for which by contrast there exists experimental evidence, is the reaction of adsorbed atoms with graphite surfaces. In this case impinging atoms are first trapped on the surface by the chemisorption potential and thereafter may be able to undergo direct reaction with lattice carbon atoms. Bar-Nun (1975) has pointed out that such reactions on graphite grains could be astrophysically important.

In order to derive a surface reaction rate for a given atom species the surface reaction must be considered in conjunction with the competing mechanism of surface recombination of these atoms. If the time for recombination of an atom is shorter than the time required for a surface reaction to take place, then the reaction rate will be much reduced. Barlow & Silk (1977) have derived a relation for $T_g(\text{react, i})$, the critical grain temperature above which reaction of an atom of species i with the graphite surface takes place faster than recombination with H atoms

$$T_g(\text{react, i}) = [E_{\text{react}}(\text{i})/k]/\ln(\nu_0 \tau_s)$$

where $E_{\text{react}}(\text{i})$ is the activation energy for reaction of atom i with graphite (equal to 0.24 eV for H atoms and 0.34 eV for O atoms), k is Boltzmann's constant, and $\nu_0 = 10^{13}/\text{s}$ is the surface vibration frequency of a chemisorbed atom. τ_s, the mean time between successive H atoms sticking to a grain surface, is given by

$$\tau_s = (\pi a^2 \bar{v}_H S_H n_H)^{-1}$$

where a is the grain radius and $\bar{v}_H$, S_H and n_H are the mean thermal velocity, sticking probability and number density of gas phase H atoms. Following Barlow & Silk (1977), $S_H = 1$ is taken for $T_{\text{gas}} \lesssim 100\,\text{K}$ and $S_H = 10^{-2}$ for $T_{\text{gas}} = 10^4\,\text{K}$, with some uncertainty in the latter value. Thus in a H II region with $T_{\text{gas}} = 10^4\,\text{K}$, we obtain $T_g(\text{react, H}) = 64$ and 71 K for $n_H = 10$ and $10^3\,\text{cm}^{-3}$, respectively, and $T_g(\text{react, O}) = 90$ and 100 K for $n_H = 10$ and $10^3\,\text{cm}^{-3}$, respectively. In a warm molecular cloud with $T_{\text{gas}} = 100\,\text{K}$ and $n_H = 1\,\text{cm}^{-3}$ ($n_H/n \sim 10^{-3}$), $T_g(\text{react, H}) = 64\,\text{K}$ and $T_g(\text{react, O}) = 90\,\text{K}$.

Provided $T_g > T_g(\text{react, H})$, the rate of decrease of mass of a graphite grain, $|dm_g/dt|$, due to surface reactions with H atoms will be given by

$$\left|\frac{dm_g}{dt}\right| = 4\pi a^2 \rho_g \left|\frac{da}{dt}\right| = \frac{n_H}{4} S_H \pi a^2 \bar{v}_H m_C$$

where $\rho_g = 2.2\,\text{g cm}^{-3}$ is the mass density of graphite and m_C is the mass of a carbon atom. The factor of 1/4 on the right-hand side arises because four H atoms are needed on average to remove one lattice atom. Thus, provided $T_g > T_g(\text{react, H})$, the time $\tau_{\text{dest}}(\text{H})$ for the destruction of a graphite grain by H atom surface reactions is given by

$$\tau_{\text{dest}}(\text{H}) = \frac{a}{|da/dt|} = \frac{16\rho_g a}{n_H S_H \bar{v}_H m_C}.$$

For a graphite grain radius of $a = 1.5 \times 10^{-6}\,\text{cm}$ we obtain $\tau_{\text{dest}}(\text{H}) = (8.4 \times 10^{10}/n_H \bar{v}_H S_H)\,\text{yr}$. Thus, in a warm molecular cloud with $T_g \sim T_{\text{gas}} = 100\,\text{K}$, $\tau_{\text{dest}}(\text{H}) = 6 \times 10^5/n_H$ yr. In a H II region [with $T_g > T_g(\text{react, H})$] $\tau_{\text{dest}}(\text{H}) \approx 6 \times 10^6/n_H$ yr. The lifetime in a H II region may be uncertain by up to a factor of ten due to uncertainties in S_H for $T_{\text{gas}} \sim 10^4\,\text{K}$ (*cf.* Barlow & Silk 1977).

Even taking into account uncertainties in S_H, the lifetime of sufficiently warm graphite grains will be less than the lifetime of a H II region in which they are immersed. Such a destruction mechanism could provide an explanation for the weakness of the 2175 Å extinction feature towards certain stars immersed in H II regions, e.g. the θ Ori system in the Orion nebula (Bless & Savage 1972), and near the 30 Doradus nebula region of the Large Magellanic Cloud (Borgman, van Duinen & Koornneef 1975). Pottasch, Wesselius & van Duinen (1976) have used the strength of the 2175 Å extinction feature towards η Car to derive an estimate of E_{B-V} towards that object. They find $E_{B-V} = 0.53$ mag, comparable to the extinction suffered by nearby stars but significantly less than the values derived from the observed ratios of nebular lines in η Car. I would suggest that the reason for the discrepancy lies in the fact that the graphite grains originally present in the η Car H II region have been destroyed (infrared observations indicate dust temperatures $\gtrsim 150$ K). Thus only foreground interstellar material would contribute to the 2175 Å graphite feature, explaining why the value of E_{B-V} derived from the feature is the same as for nearby systems not immersed in the η Car infrared source. Aitken *et al.* (1977) have derived $A_V = 3.8$ mag toward the nebula from the ratio of the hydrogen Bα and Hγ lines, in good agreement with Pagel's (1969) determination of $E_{B-V} = 1.2$ mag from the [Fe II] lines. Thus, with a foreground extinction of $A_V \approx 1.5$ mag, the extinction internal to the η Car nebula is $A_V \approx 2.3$ mag. The absence of any 2175 Å extinction attributable to extinction within the η Car nebula might be taken as additional evidence in support of the identification of the feature with graphite grains.

Besides θ Ori, other stars in the survey of Savage (1975) which had abnormally weak 2175 Å extinction features were σ Sco, NU Ori and ρ Oph. The last star is in a dense cloud and work by Carrasco, Strom & Strom (1973) has shown that some of the grains inside the cloud have accreted ice mantles. Since Gilra (1972) has predicted that even a small coating on graphite grains would destroy the 2175 Å feature, its weakness towards ρ Oph would appear to be due to that cause. However, NU Ori is in the H II region M43 and σ Sco is also immersed in a prominent H II region, suggesting that graphite grain destruction by surface reactions is responsible for the weakness of their 2175 Å extinction features.

No surface reactions will take place in diffuse interstellar clouds or in the inter-cloud medium, due to graphite grain temperatures being too low in those situations ($\lesssim 33$ K; Leung 1975). The localized destruction of graphite grains in young H II regions and in the cores of warm molecular clouds should not have a significant effect on the overall abundance of graphite grains in the interstellar medium due to the rarity of the birth of the O stars required for significant localized destruction. However better statistics on the frequency of situations with grain temperatures $\gtrsim 60$ K are required before this statement can be made definitive.

The question also arises of whether grain surface reactions could have an influence on the formation of graphite grains in circumstellar environments. In an atmosphere consisting of atomic or ionized hydrogen, grain surface reactions would be expected to destroy graphite grains as rapidly as they could condense. On the other hand, if hydrogen was in the molecular form then there would be no effect on graphite grains, since, as discussed by Barlow & Silk (1977), H_2 has an extremely low sticking probability and a negligible reaction rate. Free oxygen atoms would not be expected either in such late-type atmospheres, since in a carbon-rich atmosphere, such as appears to be required for graphite formation, oxygen will be tied up in CO molecules. Thus graphite grains should not appear around stars with spectral types earlier than the point where the transition takes place from atmospheres with molecular H_2 regions to entirely atomic hydrogen atmospheres.

Excess infrared emission observed from certain early-type stars has been interpreted as possibly being due to emission from circumstellar graphite grains, e.g. for the case of Wolf–Rayet nuclei of planetary nebulae (Cohen & Barlow 1974) and for certain Population I late WC-type Wolf–Rayet stars (Cohen, Barlow & Kuhi 1975). Interestingly, such stars have helium-rich and hydrogen-deficient atmospheres, only upper limits of [H]/[He] $\lesssim 0.1$ usually being obtainable for the hydrogen abundance in Wolf–Rayet stars (Rublev 1972; Smith 1973; Nugis 1973). Thus oxygen atoms (ions) will be the principal destruction agents for graphite grains around such stars. The lifetime of a graphite grain of radius a against destruction by O atoms is

$$\tau_{\mathrm{dest}}(0) = \frac{8\rho_{\mathrm{g}} a}{n_0 \bar{v}_0 S_0 m_{\mathrm{C}}}$$

where it is assumed that two oxygen atoms are required for the removal of one lattice atom (for the grain temperatures of $T_g \sim 1000\,\mathrm{K}$ derived by Cohen *et al.* (1975) for WC 9 stars, the resultant molecules will be rapidly evaporated, according to the results of Marsh, O'Hair & Wynne-Jones (1969)). n_0, $\bar{v}_0$ and S_0 are the number density, mean thermal velocity and sticking probability of gas phase oxygen atoms (ions). From Cohen *et al.* (1975), we have that graphite grains around WC 9 stars are at a mean distance of $10^{15}\,\mathrm{cm}$. With a flux of helium atoms at that distance of $6 \times 10^{13}\,\mathrm{cm^{-2}/s}$, an expansion velocity of 600 km/s and an abundance ratio of $[\mathrm{He}]/[\mathrm{O}] = 10^2$ (Nugis 1973) we find $n_0 = 10^4\,\mathrm{cm^{-3}}$. Taking $a = 5 \times 10^{-6}\,\mathrm{cm}$ and $T_{\mathrm{gas}} = 10^4\,\mathrm{K}$ we obtain $\tau_{\mathrm{dest}}(\mathrm{O}) = 35/S_0\,\mathrm{yr}$. Thus even for the maximum value of $S_0 = 1$ we find that $\tau_{\mathrm{dest}}(\mathrm{O}) = 35\,\mathrm{yr}$, in which time a grain travelling at 600 km/s would have travelled a further $7 \times 10^{16}\,\mathrm{cm}$, with a resultant drop in the O atom number density by a factor of 5000, and a concomitant increase in the derived grain lifetime. Thus destruction of graphite grains by surface reactions with atoms should be of no importance in the atmospheres of WC 9 and other hydrogen deficient stars such as R Cor Bor stars.

2 The destruction of grains by grain–grain collisions during cloud collisions

2.1 INTRODUCTION

Oort & Van de Hulst (1946) proposed that the growth of ice grains could be balanced by their destruction by grain–grain collisions during random collisions between interstellar clouds. In their model the steady growth of an ice grain would be terminated by its complete evaporation during a collision with a grain from the cloud being penetrated. To begin with, the treatment of Oort & Van de Hulst is briefly summarized.

The minimum relative velocity, v_{min}, required for complete evaporation of two colliding grains was obtained as follows. During the head-on inelastic collision of two grains of mass m_g and m'_g, and radii a and a', their kinetic energy of relative motion, with reduced mass $m_g m'_g/(m_g + m'_g)$, is transformed into thermal energy. If this energy is greater than the sum of the heats of evaporation of the two grains, then complete evaporation can occur. Therefore

$$\frac{1}{2}\frac{m_g m'_g}{(m_g + m'_g)}\, v_{\mathrm{min}}^2 = (m_g + m'_g)\, L \tag{1}$$

where L is the heat evaporation (sublimation energy) per unit mass of the grain material. If $a'/a = x$, then $v_{\mathrm{min}} = \sqrt{2L}\,(x^{3/2} + x^{-3/2})$. The simple case of $a = a'$ gives $v_{\mathrm{min}} = \sqrt{8L}$, and v_{min} will be larger if $a \neq a'$. Oort & Van de Hulst took $L \approx 1 \times 10^{10}\,\mathrm{erg/g}$, which gives $v_{\mathrm{min}} = 2.8\,\mathrm{km/s}$. (The values of v_{min} for $\mathrm{MgSiO_3}$, iron and graphite grains are 5.8, 7.6 and 21.5 km/s, respectively.)

The distance D which a grain could penetrate into a cloud before slowing to below the relative velocity v_{min} was obtained from the equation of motion of the grain

$$m_g \frac{dv}{dt} = -\pi a^2 \rho v^2 \tag{2}$$

which gives

$$D = \frac{4a\rho_g}{3\rho} \ln\left(\frac{v_0}{v_{\mathrm{min}}}\right). \tag{3}$$

Here ρ_g is the mass density of the grain material, ρ is the mass density of the cloud, and v_0 is the initial velocity of the grain relative to the cloud being penetrated. For typical assumed parameters of $a = 10^{-5}$ cm, $\rho_g = 1\,\mathrm{g\,cm^{-3}}$, $\rho = 3 \times 10^{-23}\,\mathrm{g\,cm^{-3}}$ and $v_0 = 22.5$ km/s, a value of $D \sim 0.3$ pc was derived. The probability of destruction of a grain during a cloud collision was given by $P_{\mathrm{dest}} = n_g \sigma D$, where N_g is the number density of grains in the cloud and $\sigma = 4\pi a^2$ was taken as the cross section for grain–grain collisions. With $n_g = 7.6 \times 10^{-11}\,\mathrm{cm^{-3}}$ these assumptions gave $P_{\mathrm{dest}} = 0.87$, and with a time between cloud collisions of 9×10^6 yr a lifetime against destruction of $\tau_{\mathrm{dest}} = 10^8$ yr was obtained, nicely balancing the expected grain growth to $\sim 10^{-5}$ cm in this period. The next section investigates how the conclusions of Oort & Van de Hulst are modified when the full shock wave structure at the interface between two colliding clouds is considered.

2.2 CLOUD COLLISIONS ALONG MAGNETIC FIELD LINES

For the standard cloud parameters of Spitzer (1968) ($n = 10\,\mathrm{cm^{-3}}$, radius $R = 7$ pc and an rms space velocity of 14 km/s), the mean relative velocity of collision of two clouds will be $\sqrt{2} \times 14\,\mathrm{km/s} = 20\,\mathrm{km/s}$. Upon collision a shock wave will propagate back into each cloud. From the point of view of the analysis of grain dynamics in the shocked region, it is important to know whether the shocks must be treated as adiabatic or isothermal. Stone (1970) has calculated numerically the hydrodynamical evolution of two colliding Spitzer clouds and finds that initially the reflected shocks are adiabatic, with the transition to isothermality taking place between 2–3×10^4 yr after initial cloud contact. More detailed calculations by Aannestad (1973) give a transition timescale of a few times 10^3 yr. The treatment given here assuming purely adiabatic shocks, shows that grains are only capable of being destroyed for $< 2 \times 10^4$ yr after initial cloud contact. Alternative calculations, carried out for the case of purely isothermal shocks and discussed later in this section, lead to no significant changes in the destruction probabilities derived for the case of adiabatic shocks.

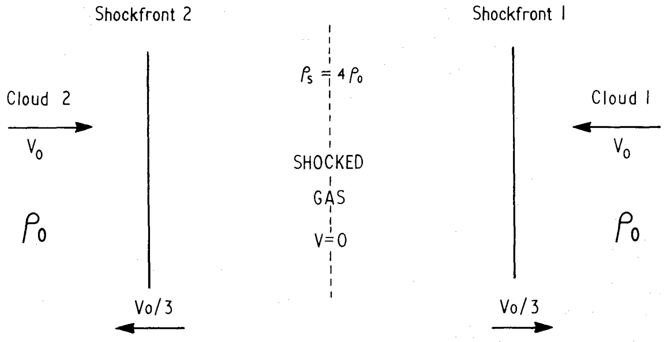

Figure 1. The adiabatic shock structure at the interface between two identical clouds, of initial density ρ_0, which are colliding with a relative velocity of $2v_0$.

The resistance to the motion of a small sphere in a gaseous medium has been considered by Baines, Williams & Asebiomo (1965). If v_T is the mean thermal velocity of the gas [$v_T = (8kT/\pi\mu m_H)^{1/2}$] and v is the velocity of the grain, then they show that the resistance by the gas is given by $R_s = \pi a^2 \rho v^2$ only for $v \gg v_T$. This condition is satisfied for a grain passing through an isothermally shocked region or through the unshocked portion of the opposite cloud, but not for a grain passing through the hot shocked gas behind an adiabatic shock. For the latter case it can be shown that $v_T^2 = (8/3\pi)v_0^2$, where v_0 is the velocity jump across the shock. v_0 is also equal to the initial grain velocity as it enters the shocked region, so initially $v/v_T = \sqrt{3\pi/8}$, and from Baines *et al.* the approximation for specular reflection,

$R_s = (4/3)\pi a^2 \rho v v_T$, is used. This approximation underestimates the drag by 30 per cent initially but becomes more and more accurate as v decreases. Fig. 1 illustrates schematically the interface region between two identical colliding clouds, designated 1 and 2. For a strong adiabatic shock, the ratio of gas densities in the shocked and unshocked regions, ρ_s/ρ_0, is equal to $(\gamma+1)/(\gamma-1)$ (*cf.* Spitzer 1968), which for $\gamma = 5/3$ gives $\rho_s/\rho_0 = 4$. If u_s and u_0 are the velocities of the shocked and unshocked gas relative to the shock front, then from conservation of matter through the front $u_s/u_0 = 1/4$. Since the shocked regions of each cloud must be at rest with respect to each other we also have the condition $u_s - u_0 = v_0$, where v_0 is the velocity of each cloud in the frame of the shocked gas. Therefore $u_0 = (4/3)v_0$ and $u_s = (1/3)v_0$, i.e. a shock front moves into each cloud with velocity $v_0/3$.

The equation of motion of a grain in the shocked region will be

$$\frac{4}{3}\pi a^3 \rho_g \frac{dv}{dt} = -\frac{4}{3}\pi a^2 \rho_s v_T v \tag{4}$$

which can be integrated to give

$$t = \frac{a\rho_g}{\rho_s v_T}\ln\left(\frac{v_0}{v}\right) \tag{5}$$

where v_0 is the initial grain velocity relative to the shocked gas and v is the velocity at time t.

Consider grain 1 which is initially a distance L_1 behind the front of cloud 1. The initial velocity of this grain in the frame of the shocked gas is v_0 and on entering the shocked region the grain will have a velocity $v_1(D_1)$ which can be derived from (4) to be given by

$$v_1(D_1) = v_0 - \frac{\rho_s v_T}{a\rho_g} D_1 \tag{6a}$$

where D_1 is the distance travelled in the shocked region. Similarly a grain from cloud 2 which has travelled a distance D_2 into the shocked region will have a velocity $v_2(D_2)$ given by

$$v_2(D_2) = v_0 - \frac{\rho_s v_T}{a\rho_g} D_2. \tag{6b}$$

Consider a grain from cloud 2, an initial distance L_2 behind the front of that cloud, which when level with grain 1 in the shocked region has a velocity $v_2(D_2)$ such that $v_1(D_1) + v_2(D_2) = v_{\min}$, i.e.

$$2v_0 - \frac{\rho_s v_T}{a\rho_g} D_1 - \frac{\rho_s v_T}{a\rho_g} D_2 = v_{\min}. \tag{7}$$

At the moment of initial cloud contact the separation of the two grains is equal to $L_1 + L_2$. This distance must be equal to the sum of the distances travelled by the two grains before they meet, i.e. to the sum of D_1 and D_2 plus the distances moved by each grain before meeting the shock front. Therefore

$$L_1 + L_2 = D_1 + D_2 + v_0\left[\frac{L_1}{(4v_0/3)} + \frac{L_2}{(4v_0/3)}\right]$$

which gives

$$L_1 + L_2 = 4D_1 + 4D_2. \tag{8}$$

The grains are level with each other at a time τ after initial cloud contact with

$$\tau = \frac{L_1}{(4v_0/3)} + \frac{a\rho_g}{\rho_s v_T} \ln\left[\frac{v_0}{v_1(D_1)}\right] \tag{9a}$$

$$\tau = \frac{L_2}{(4v_0/3)} + \frac{a\rho_g}{\rho_s v_T} \ln\left[\frac{v_0}{v_2(D_2)}\right]. \tag{9b}$$

The first term on the right-hand side of each equation is the time taken by each grain to reach the shock front which has been reflected into its cloud, and the second term is the time taken to travel from the shock front to level with the other grain.

Equating (9a) to (9b), substituting for L_2 from (8), for $v_1(D_1)$ and $v_2(D_2)$ from (6), and for D_2 from (7), gives, after some rearranging

$$\frac{L_1}{K} = \sqrt{\frac{3\pi}{8}}\left\{(4-2c) + \frac{2}{3}\ln\left[\frac{\sqrt{3\pi/8} - (D_1/K)}{(D_1/K) - \sqrt{3\pi/8}\,(1-c)}\right]\right\} \tag{10}$$

where $K = a\rho_g/\rho_s$, $c = v_{\text{min}}/v_0$, and $v_0/v_T = \sqrt{3\pi/8}$. A similar equation for L_2 can also be obtained:

$$\frac{L_2}{K} = \sqrt{\frac{3\pi}{8}}\left\{(4-2c) - \frac{2}{3}\ln\left[\frac{\sqrt{3\pi/8} - (D_1/K)}{(D_1/K) - \sqrt{3\pi/8}(1-c)}\right]\right\}. \tag{11}$$

Now if grain 1 starts at an initial distance behind the front of cloud 1 greater than some critical value $L_1(\text{max})$, then it will never meet a grain from cloud 2 with a relative velocity greater than v_{min}. L_1 is equal to $L_1(\text{max})$ when $L_2 = 0$ [for $L_1 > L_1(\text{max})$, L_2 would be negative]. Therefore equating L_2/K in (11) to zero and substituting into (10) we obtain

$$\frac{L_1(\text{max})}{K} = 4\sqrt{\frac{3\pi}{8}}(2-c). \tag{12}$$

Therefore in any given cloud collision only a fraction $f = L_1(\text{max})/2R$ of the grains in a cloud will have a chance of meeting grains from the other cloud with sufficient relative velocity to cause their mutual destruction. Thus the derived mean lifetime of grains will be increased by a factor of $1/f$ over the lifetime that would have been derived by assuming that the mean destruction probability $\langle P_{\text{dest}}\rangle$ for grains with $L_1 < L_1(\text{max})$ was applicable to all grains in the cloud.

To investigate the dependence of $L_1(\text{max})$ upon likely values of the parameter c consider the three alternative binding energies for ice grains discussed in Section 1 of Paper I. (i) $L = 5.6 \times 10^9$ erg/g (0.1 eV per molecule). For $v_0 = 10$ km/s (corresponding to the relative cloud velocity of 20 km/s) this gives $c = 0.21$ and $L_1(\text{max}) = 7.8\,K$. (ii) $L = 1 \times 10^{10}$ erg/g (0.18 eV per molecule); giving $c = 0.28$ and $L_1(\text{max}) = 7.5\,K$ for $v_0 = 10$ km/s. (iii) $L = 2.1 \times 10^{10}$ erg/g (0.37 eV per molecule); giving $c = 0.41$ and $L_1(\text{max}) = 6.9\,K$ for $v_0 = 10$ km/s. The dependence of $L_1(\text{max})$, and thus of f, on the grain binding energy can therefore be seen to be very weak. Similarly it is found in calculating $\langle P_{\text{dest}}\rangle$ that the dependence of this quantity on the parameter c is also relatively weak. Therefore, only the results for the representative intermediate case of $L = 1 \times 10^{10}$ erg/g ($c = 0.28$) will be presented. With $R = 7$ pc and $K = 1.1 \times 10^{17}$ cm (appropriate for $a = 10^{-5}$ cm, $\rho_g = 1$ g cm^{-3} and ρ_s corresponding to four times the unshocked H nucleus number density of $n = 10$ cm^{-3} with a 10 per cent helium abundance by number relative to hydrogen), this gives $f = 1/54$.

For the purpose of calculating the mean destruction probability the region between $L_1 = 0$ and $L_1 = L_1(\max)$ can be divided into three zones.

Zone A. For $L_1 < L_1(\min)$ grains from cloud 1 can enter the unshocked portion of cloud 2. The value of $L_1(\min)$ can be obtained from the condition that a grain starting at $L_1(\min)$ be travelling at the same velocity as shock front 2 (i.e. $v_0/3$) when it reaches that shock front, therefore

$$\frac{v_0}{3} = v_0 - v_T \cdot \frac{D_1}{K}. \tag{13}$$

When the grain reaches shock front 2, the distance D_1 which it has travelled in the shocked region will be equal to the separation of the shock fronts when the grain crossed shock front 1, plus the distance moved by shock front 2 while the grain was slowing from v_0 to $v_0/3$. Therefore

$$D_1 = \frac{L_1(\min)}{2} + \frac{v_0}{3} \cdot \frac{K}{v_T} \ln\left(\frac{v_0}{v_0/3}\right). \tag{14}$$

Combining (13) and (14) we obtain

$$\frac{L_1(\min)}{K} = \frac{2}{3}\sqrt{\frac{3\pi}{8}}\,\{2 - \ln 3\} \tag{15}$$

i.e. $L_1(\min) = 0.65\,\mathrm{K}$.

Zone B. This zone extends from $L_1(\min)$ to $L_1(\mathrm{mid})$, where $L_1(\mathrm{mid})$ is the value of L_1 for which a grain at shock front 1 encounters grains originally from $L_2(\min)$ $[L_2(\min) = L_1(\min)]$. These grains from $L_2(\min)$ will be travelling at velocity $v_0/3$ at shock front 1. Substituting $L_2 = L_2(\min)$ and $D_1 = 0$ into (8) we obtain

$$\frac{L_1(\mathrm{mid})}{K} + \frac{2}{3}\sqrt{\frac{3\pi}{8}}\,\{2 - \ln 3\} = 4D_2/\mathrm{K} \tag{16}$$

and with

$$v_2(D_2) = v_0 - v_T\frac{D_2}{K} = \frac{v_0}{3} \tag{17}$$

we find

$$\frac{L_1(\mathrm{mid})}{K} = \frac{2}{3}\sqrt{\frac{3\pi}{8}}\,\{2 + \ln 3\} \tag{18}$$

i.e. $L_1(\mathrm{mid}) = 2.2\,\mathrm{K}$.

Zone C. This zone extends from $L_1(\mathrm{mid})$ to $L_1(\max)$. Note that a grain from $L_1(\max)$ only reaches a grain from cloud 2 with sufficient relative velocity for destruction just as its velocity $v_1(D_1)$ reaches $v_{\min}$ (the grains from cloud 2 are at rest at that point). Thus the grain destruction probability falls to zero as L_1 goes from $L_1(\mathrm{mid})$ to $L_1(\max)$.

The destruction probability for a grain from cloud 1 is given by

$$P_{\mathrm{dest}} = \int n_g\,\sigma(v_1 + v_2)\,dt \tag{19}$$

where v_2 is the velocity of the grains from cloud 2 which are passing grain 1 at a particular instant, n_g is the number density of those grains, and σ is the cross section for grain–grain collisions. The limits of this integral are from t corresponding to $v_1 = v_0$ (or time t corresponding to grain 1 first meeting grains from cloud 2, whichever is appropriate) to t corresponding to $(v_1 + v_2) = v_{\min}$.

If $n_g(0)$ is the number density of grains in an unshocked standard cloud, then $n_g = \psi n_g(0)$, where

$$\psi = \frac{4v_0/3}{v_2 + v_0/3}. \tag{20}$$

The parameter ψ describes the change in the number density of grains from cloud 2 as they slow in the shocked region from $v_2 = v_0(\psi = 1)$ to $v_2 = 0\,(\psi = 4)$.

Average values of the quantity P_{dest} have been calculated for each of the three zones. This was done by computing P_{dest} for appropriately spaced intervals in L_1 in each zone and then taking the average to obtain $\langle P_{\text{dest}} \rangle$ for the zone. For the grains in Zone A which enter the unshocked portion of cloud 2 the appropriate gas resistance term, $R_s = \pi a^2 \rho v^2$, was used whilst they remained in the unshocked region. Allowance was made for the small increase in P_{dest} for grains near the front of cloud 1. It can be shown that, in the absence of a transverse magnetic field, grains will not be overtaken or destroyed by grains coming from further back in their own cloud.

The average destruction probabilities for each of the three zones, for $c = 0.28$, were found to be: $\langle P_{\text{dest}}(\text{A}) \rangle = 7.2K\sigma n_g(0)$; $\langle P_{\text{dest}}(\text{B}) \rangle = 5.7K\sigma n_g(0)$; and $\langle P_{\text{dest}}(\text{C}) \rangle = 2.2K\sigma n_g(0)$.

The average destruction probability $\langle P_{\text{dest}} \rangle$ for the whole region lying between $L_1 = 0$ and $L_1 = L_1(\max)$ is thus equal to $3.4K\sigma n_g(0)$.

To obtain an appropriate value for $n_g(0)$, a dust to gas mass ratio of 10^{-2} is assumed. This corresponds to approximately two thirds of all C, N and O atoms being locked up in ice grains and so is a good upper limit. We then have $n_g(0) = 10^{-2}\rho_0/[(4/3)\pi a^3 \rho_g]$. $\sigma = 4\pi a^2$ is assumed, as in Oort & Van de Hulst [1946, but see below]. Since $K = a\rho_g/\rho_s$, with $\rho_s = 4\rho_0$, we thus obtain

$$P_{\text{dest}} = 3.4\,\frac{a\rho_g}{4\rho_0}\,4\pi a^2\,\frac{10^{-2}\rho_0}{(4/3)\pi a^3 \rho_g} = 2.5 \times 10^{-2}. \tag{21}$$

The mean lifetime against destruction by this mechanism for grains in clouds will be

$$\tau_{\text{dest}} = \frac{\tau_{\text{cc}}}{P_{\text{dest}} f} \tag{22}$$

where τ_{cc} is the time interval between cloud–cloud collisions, which the standard cloud parameters of Spitzer (1968) give to be $\tau_{\text{cc}} = 6.5 \times 10^6$ yr. With $P_{\text{dest}} = 2.5 \times 10^{-2}$ and $f = 1/54$ we obtain $\tau_{\text{dest}} = 1.4 \times 10^{10}$ yr, i.e. greater than, or of the same order as, the age of the Galaxy. It can therefore be concluded that the classical Oort–van de Hulst grain–grain collision mechanism is unimportant as a destruction mechanism for ice grains in clouds.

As mentioned earlier in this section, there exists the possibility that, towards the end of the path length over which the destruction of decelerating grains may occur, they may be travelling through a region which has cooled significantly, so that conditions would then correspond to those of an isothermal shock. In order to investigate if this might have any effect on the above results, the calculations were repeated assuming that the shocks were isothermal right from the moment of initial cloud contact. For this extreme case similar equations to (4) to (11) may be derived using the resistance term $R_s = \pi a^2 \rho v^2$, and the results can be summarized as follows. For $L_2 = 0$ it is found that

$$\frac{L_1'(\max)}{K'} = M^2\left\{\frac{D_1'}{K'} + \left[\frac{1}{c - \exp(D_1'/K')}\right]\right\} \tag{23}$$

where

$$M^2\left\{\frac{D_1'}{K'} + \ln\left[\frac{1}{c - \exp - (D_1'/K')}\right]\right\} = \frac{1}{1 - (1/M^2)}\left\{\frac{1}{c - \exp - (D_1'/K')} - \frac{1}{\exp - (D_1'/K')}\right\} \tag{24}$$

M is the Mach number of the shock and $K' = 4a\rho_g/3\rho_0 M^2$. For a typical Mach number of $M = 10$ it is found that $L_1'(\max)$, and thus f, is five times the value derived for the case of an adiabatic shock. However, for the case of an isothermal shock the distances over which grains are decelerated (and over which they may be destroyed) are approximately a factor of $M^2/4$ less than those appropriate for the case of an adiabatic shock (i.e. a factor of K/K' less). This decrease in the deceleration distance is not adequately compensated for by an increase in the parameter ψ' [analogous to the parameter ψ in (20)] which describes the increase in the density of grains from cloud 2 over their density in the unshocked cloud, as they slow down in the shocked region:

$$\psi' = \frac{v_0/[1 - (1/M^2)]}{v_2 + v_0/(M^2 - 1)}. \tag{25}$$

Only for $v_2 = 0$ does $\psi'/\psi = M^2/4$. Averaged over the run of values of v_2 encountered by grains from cloud 1 it is found that, for $M = 10$, $\langle \psi'/\psi \rangle \simeq 0.14M^2/4$. The average destruction probability for grains with $L_1 < L_1'(\max)$ in the isothermal case is thus a factor of seven less than that for grains with $L_1 < L_1(\max)$ in the adiabatic case. So if isothermal shocks are assumed, the lifetime against destruction for ice grains in clouds is found to be a factor of 7/5 larger than that found for the case of adiabatic shocks. The conclusions reached for the latter case are thus unchanged. Aannestad (1973) in a detailed numerical study of gas and grain evolution in two clouds with $n \sim 10\,\mathrm{cm}^{-3}$, colliding with relative velocity ~ 20 km/s, found a grain–grain collision destruction probability similar to that derived here for the general case.

2.3 THE EFFECT OF TRANSVERSE MAGNETIC FIELDS

Another destruction mechanism involving grain–grain collisions has been discussed by Jura (1976); Spitzer (1976) and Shull (1977), namely the collision in a shock-front of grains from the same cloud, due to their spiralling around transverse magnetic lines of force. Shull (1977) has considered the detailed hydromagnetics of the problem and has derived grain destruction probabilities which are found to be reproduced with fair accuracy by the approximate formula of Jura (1976)

$$P_{\mathrm{dest}} = 0.02\left(\frac{\sigma}{\pi a^2}\right)\ln(v_0/v_{\min}) \tag{26}$$

where σ is the cross section for destructive grain–grain collisions between grains with the same radius a. As in Section 2.1, v_0 is the initial grain velocity and $v_{\min}$ is the minimum relative velocity required for complete grain destruction in a head-on collision.

However, consider a collision which is not head-on, between grains with a relative velocity v_{rel}. The loss of kinetic energy ΔE, in a perfectly inelastic collision between grains of mass m_{g} and m'_{g}, is given by

$$\Delta E = \frac{1}{2}\frac{m_{\mathrm{g}}m'_{\mathrm{g}}}{(m_{\mathrm{g}}+m'_{\mathrm{g}})} v_{\mathrm{rel}}^2 \sin^2\theta \tag{27}$$

where the collision angle θ is the angle between the line of centres and the perpendicular to the direction of relative motion. Thus $\theta = 0$ for a grazing collision. Comparing (27) with (1), it can be seen that the minimum relative velocity, v'_{min}, required for complete evaporation of both grains, is given by

$$v'_{\mathrm{min}} = v_{\mathrm{min}}/\sin\theta \tag{28}$$

where v_{min} is the minimum velocity required in the case of a head-on collision. It is still assumed that all of the dissipated kinetic energy goes towards producing evaporation, with none going towards producing fragmentation.

The differential cross section, $\sigma(\theta)$, for grain–grain collisions at an angle θ, is given by

$$\sigma(\theta) = 4\pi a^2 \cos^2\theta. \tag{29}$$

Thus, in the general case of grains colliding at all collision angles θ between 0 and $\pi/2$, equation (26) is modified to

$$P_{\mathrm{dest}} = 0.02\left[\frac{2}{\pi}\left\{4\int_{\sin^{-1}(v_{\mathrm{min}}/v_0)}^{\pi/2} \ln\left(\frac{v_0\sin\theta}{v_{\mathrm{min}}}\right)\cos^2\theta\, d\theta\right\}\right]. \tag{30}$$

Shull (1977) finds that if $v_0 \gtrsim 50\,\mathrm{km/s}$, the resultant ionization of the gas and greater frictional drag on the grains reduces the grain destruction probability to negligible values. Thus, in computing the lifetime of grains against this mechanism in supernova shock-fronts, the upper and lower limits for the initial shock velocity v_0 will be set equal to 50 and 14 km/s, respectively; the lower limit corresponding to the velocity at which a remnant merges with the mean random velocity of interstellar clouds. As in Section 2.8 of Paper I a mean initial supernova energy divided by local interstellar density, $E_0/n = 3 \times 10^{50}\,\mathrm{erg\,cm^3}$, is adopted, along with equation (26) of Chevalier (1974) for the radius of a remnant with expansion velocity v_0. The radii of remnants with $v_0 = 50$ and 14 km/s are found to be 25.3 and 44.7 pc, respectively. The volume weighted grain destruction probabilities P_{dest}, for ice grains with $H_{\mathrm{s}} = 0.1$, 0.2 and 0.37 eV, are found to be 0.044, 0.035 and 0.024, respectively. $\mathrm{MgSiO_3}$ silicate grains with $v_{\mathrm{min}} = 5.8\,\mathrm{km/s}$ have a volume weighted P_{dest} equal to 0.015 and iron grains with $v_{\mathrm{min}} = 7.6\,\mathrm{km/s}$ have a volume weighted P_{dest} equal to 0.010. These destruction probabilities correspond to values of $(\sigma/\pi a^2)$, in equation (26), which for $v_0 = 50\,\mathrm{km/s}$ range from 1.28 for $v_{\mathrm{min}} = 2.09\,\mathrm{km/s}$ to 0.94 for $v_{\mathrm{min}} = 7.6\,\mathrm{km/s}$; and for $v_0 = 14\,\mathrm{km/s}$ range from 0.94 for $v_{\mathrm{min}} = 2.09\,\mathrm{km/s}$ to 0.32 for $v_{\mathrm{min}} = 7.6\,\mathrm{km/s}$. Graphite grains with $v_{\mathrm{min}} = 21.5\,\mathrm{km/s}$ have a negligible destruction probability.

For calculating overall grain lifetimes against this mechanism, the supernova parameters of Section 3.6 of Paper I are adopted, i.e. $\tau_{\mathrm{SN}} = 150\,\mathrm{yr}$ and an effective galactic volume for supernova generation corresponding to a disc of radius 15 kpc and thickness 120 pc. In addition, it is assumed that grains can only be destroyed by this mechanism in half the volume into which the remnants expand, since shocks expanding parallel to magnetic lines of force lead to negligible grain–grain destruction probabilities, as shown in Section 2.2. The lifetimes against this mechanism for ice grains with $H_s = 0.1$, 0.2 and 0.37 eV are found to be 1.9, 2.5 and 3.6×10^9 yr, respectively. Silicate grains would have a lifetime of 5.7×10^9 yr, and iron grains a lifetime of 9.0×10^9 yr. These lifetimes are longer than those for destruction by sputtering in supernova shock fronts (Paper I).

If interstellar clouds do in fact collide randomly, rather than along magnetic field lines as discussed at the conclusion of Section 2.2, then grains may be destroyed by magnetic field influenced collisions in their case also. It is assumed that the initial grain velocity v_0, relative to the shocked gas, has a probability distribution, $P(v_0)$, given by

$$P(v_0)\, dv_0 = \frac{1}{b} \exp(-v_0/b)\, dv_0 \tag{31}$$

where $b = 10$ km/s for collisions between identical clouds having the one-dimensional cloud velocity dispersion of 8 km/s adopted by Spitzer (1968). In this case P_{dest} can be obtained by convolving (31) with (30), with v_0 integrated between the limits of zero and infinity. It is found that $P_{\text{dest}} = 0.021$, 0.016 and 0.010 for ice grains with $H_s = 0.1$, 0.2 and 0.3 eV, respectively, and $P_{\text{dest}} = 0.0058$ and 0.0036 for silicate and iron grains. The overall lifetime, τ_{dest}, of a grain against this mechanism will be $2\tau_{\text{cc}}/P_{\text{dest}}$, where $\tau_{\text{cc}} = 6.5 \times 10^6$ yr is the cloud–cloud collision time and the factor of two allows for collisions along field lines. Thus for ice grains with $H_s = 0.1$, 0.2 and 0.37 eV, $\tau_{\text{dest}} = 6.2 \times 10^8$, 8.1×10^8 and 1.3×10^9 yr, respectively, and for silicate and iron grains $\tau_{\text{dest}} = 2.2 \times 10^9$ and 3.6×10^9 yr.

These lifetimes are longer than those found for sputtering by supernova remnants (Paper I). Moreover, apart from the possibility that cloud collisions may take place predominantly along magnetic field lines, three other factors will tend to decrease the destruction probabilities derived above.

(a) If some fraction of the energy dissipated in grain collisions goes into fragmentation rather than evaporation, the destruction probabilities will be lowered.

(b) The destruction probabilities given by equations (26) and (29) are proportional to the dust to gas mass ratio, for which a value of 10^{-2} was assumed. Since we shall see in the next section that ice mantles on grains in diffuse clouds are destroyed by photodesorption at a much faster rate than the rate at which shocks are encountered, we are here interested primarily in the destruction of silicate and iron grains. If cosmic abundances of Mg, Si and Fe were locked up in silicate and iron-magnetite grains, the maximum dust to gas mass ratio for such grains would be $5.5\text{–}6 \times 10^{-3}$. Thus, even if silicate and iron-magnetite grains should have the same radius, the lifetimes derived above, for destruction by supernova remnants or by cloud–cloud collisions, must be multiplied by a factor of ~ 2.

(c) Finally, if as discussed by Heiles (1974), the number of clouds per kpc is intermediate between 2.5 and the value of 8 assumed above, then the lifetimes derived for destruction during cloud–cloud collisions will be increased further.

For these reasons it is concluded that grain–grain collisions are not a significant overall destruction mechanism for interstellar dust and in shock-fronts destruction by sputtering will always be more important.

3 Photodesorption

Photodesorption may be defined as a process whereby an adsorbed particle is desorbed from a surface by a photon via a *quantum* process. This definition excludes normal thermal desorption caused by bulk heating of a solid.* Watson & Salpeter (1972) were the first to consider in detail the process of photodesorption of molecules from interstellar grain surfaces. Following L. T. Greenberg (1973), the term photodesorption will be used here to cover not only the removal of adsorbed particles but also the removal of surface molecules of a solid. Oort & van de Hulst (1946) included such a mechanism in their list of possible destruction mechanisms for interstellar ice grains, but at that time there existed no experimental or theoretical data on which to base estimates. A summary of the literature on photodesorption up to 1972 can be found in Greenberg (1973). I will first consider the case of photodesorption of adsorbed particles for surface coverages $\leqslant 1$ monolayer and then consider the case of particles adsorbed in multilayers (e.g. dirty-ice mantles).

Three principal mechanisms have been proposed to explain the photodesorption of physically adsorbed or chemisorbed particles from a surface.

(i) Excitation of the underlying surface and transferral of this excitation to the adsorbed particle. Such a mechanism appears to explain the desorption of particles adsorbed on some semiconducting solids, such as CdS illuminated by photons with energy greater than the band-gap of 2.4 eV (Baidyaroy, Bottoms & Mark 1971), but in general cannot explain the ubiquity of the photodesorption phenomenon which is found to occur not only for semiconductors but also for metals and insulators.

(ii) Excitation of an electron of the adsorbed particle by a photon, such that the surface-adsorbed particle system finds itself in an antibonding state (repulsive potential) and the adsorbed particle desorbs (Harrison & Schoen 1967; Watson & Salpeter 1972; Gersten, Janow & Tzoar 1975).

(iii) An adsorbed *molecule* is excited into a higher electronic state by a photon, and returns to the ground electronic state in a highly excited vibration–rotation level. Some of the internal kinetic energy is then converted into translational energy away from the surface by collision with surface atoms (Greenberg 1973).

Mechanism (iii) can work only for adsorbed molecules and to date no *atoms* have ever been observed to be photodesorbed.† The lack of any observed atomic photodesorption might be due to the fact that in general only photons with $\lambda \geqslant 1850$ Å have been used in experiments and it is known that for electron stimulated desorption the threshold energy for H^+ desorption from CO and H_2 co-adsorbed on tungsten is 10 eV, compared to a threshold energy of ~ 3 eV for desorption of H_2 (Jelend & Menzel 1974). However, if mechanism (iii) applied for both photodesorption and electron stimulated desorption then the H^+ observed by Jelend & Menzel could have come from the dissociation and ionization of H_2 as the H_2 was being desorbed, consistent with the much lower yield for H^+ desorption (a factor of $\sim 10^3$ less than for H_2 desorption). The threshold of 10 eV for H^+ desorption found by Jelend & Menzel is close to the energy required for dissociation of H_2 by Lyman & Werner band excitation. One photodesorption experiment has, however, used photons with $\lambda < 1850$ Å. Peavy & Lichtman (1971) irradiated adsorbed molecules on tungsten with a broad-band synchrotron radiation source generating photons of mean wavelength ~ 2000 Å,

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* Isobe (1970) has shown that ice grains will only be thermally evaporated within a distance of ~ 1 pc from an O5 star, and since evaporation will only occur at even smaller distances from later type stars, thermal evaporation will not have a significant effect on the overall abundance of ice grains in the interstellar medium, due to the low probability of a grain finding itself close enough to a hot star for mantle evaporation to occur.

† Genequand (1971) irradiated CO and CO_2 adsorbed on a nickel surface using photons with wavelength $\lambda \geqslant 2530$ Å and found a third (weak) mass spectrometric peak at atomic weight 16 which might have been due to atomic oxygen or impurity CH_4.

but with a tail extending down to 400–800 Å. CO_2, CO and H_2 were desorbed, but no atoms were found to be desorbed. H_2 is known to chemisorb dissociatively on tungsten (Wise & Wood 1967) and since, according to the data of Peavy & Lichtman, only a tenth of a monolayer of gas was adsorbed, most of the hydrogen on the surface would be expected to be in the atomic form. The failure to observe any photodesorbed atomic hydrogen could argue that mechanism (iii) was responsible for the observed photodesorption. However, further experimental evidence is required before mechanisms (ii) and (iii) can definitely be discriminated between.

The available experimental data on photodesorption yields and cross sections are now summarized, where the photodesorption yield, Y_{pd}, is the number of adsorbed particles ejected per incident photon, and each adsorbed particle has a cross section σ_{pd} for desorption by an incident photon. A standard mean surface area per adsorbed particle of 10^{-15} cm^2 is assumed, so that for a fractional surface coverage θ, $\sigma_{pd} = (10^{-15}/\theta)\, Y_{pd}$ cm^2.

Peavy & Lichtman (1971) found $\sigma_{pd} = 8 \times 10^{-21}$ cm^2 for irradiation of CO_2, CO and H_2 on tungsten by photons of mean wavelength $\lambda = 2000$ Å. Kronauer & Menzel (1972) found $\sigma_{pd} = 6 \times 10^{-21}$ cm^2 for irradiation by 2500 Å photons of CO_2 on nickel, with the yield falling to $Y_{pd} = 9 \times 10^{-11}$ at 3860 Å, and undetectable for $\lambda > 4000$ Å. Fabel, Cox & Lichtman (1973) found photodesorption of CO_2, CO, H_2O, CH_4 and H_2 to occur from a stainless steel surface (where stainless steel is a collection of metal oxides with perhaps Cr_2O_3 as the major constituent in the 304 stainless steel used by Fabel *et al.*). They found no photodesorption for photons with $\lambda > 3600$ Å. For 2550 Å photons a yield of $Y_{pd} = 9 \times 10^{-5}$ was found, corresponding to $\sigma_{pd} = 9 \times 10^{-20}$ cm^2 and for 1850 Å photons they found $Y_{pd} = 5.5 \times 10^{-3}$, corresponding to $\sigma_{pd} = 5.5 \times 10^{-18}$ cm^2. Greenberg (1973) irradiated various molecules which were physically adsorbed on quartz (SiO_2), using photons in the wavelength range 2000–2750 Å. He found $Y_{pd} \sim 10^{-5}$ for CS_2 ($\sigma_{pd} \sim 10^{-20}$ cm^2), $Y_{pd} \sim 10^{-6}$ for CO_2, O_2 and CO ($\sigma_{pd} \sim 10^{-21}$ cm^2) and $Y_{pd} \sim 10^{-6}$–10^{-7} for C_6H_6, C_4H_{10}, N_2, CH_4, H_2O, CH_3OH and NH_3 ($\sigma_{pd} \sim 10^{-21}$–$10^{-22}$ cm^2). Finally, a detailed theory of photodesorption of *atoms* by means of mechanism (ii) has been produced by Gersten *et al.* (1975), taking into account effects such as de-excitation of excited adsorbed atoms by surface plasmons. For assumed parameters such as a height above the surface of 2 Å, an adsorbed atom mass of $\sim 6m_H$, a surface plasmon energy of 5 eV and an incident photon energy of 6.3 eV ($\lambda = 1970$ Å), they predicted $\sigma_{pd} = 4 \times 10^{-18}$ cm^2. The agreement with the result of Fabel *et al.* (1973) may be fortuitous but indicates that mechanism (ii) cannot be ruled out.

A value of $\sigma_{pd} \approx 5 \times 10^{-18}$ cm^2 is similar to the cross sections found for electron stimulated desorption of molecules chemisorbed on metals, for electrons with energy up to ~ 100 eV, whose excitation characteristics should be similar to those of ultraviolet photons (Watson & Salpeter 1972). Jelend & Menzel (1974) found that H_2 coadsorbed with CO on tungsten had a desorption cross section of $> 10^{-16}$ cm^2 for irradiation by 100 eV electrons, and for 10 eV electron irradiation had a desorption cross section of $\sim 4 \times 10^{-17}$ cm^2. For gas-phase H_2 molecules, the total cross section (excitation, ionization, dissociation) for incident 100 eV electrons is $\sim 5 \times 10^{-16}$ cm^2 (Massey 1969), falling to a few $\times\, 10^{-17}$ cm^2 for 10–15 eV electrons. Thus the H_2 electron desorption cross sections found by Jelend & Menzel correspond closely to the electronic cross sections of gas-phase H_2 molecules. The H_2 molecules in the experiment of Jelend & Menzel were suspected to be quasi-physically absorbed on top of CO molecules, due to the low H_2 sticking probability (10^{-4}–10^{-3}), and the low H_2 adsorption energy (~ 0.3–0.5 eV), which were found in the experiment. The higher desorption cross section for physically adsorbed molecules compared with chemisorbed molecules can be explained by both mechanisms (ii) and (iii), since physically adsorbed molecules have equilibrium distances from a surface larger than those of chemisorbed particles (~ 3 Å versus 1–2 Å) and would thus have a lower probability for de-excitation by bulk electrons after absorption of a photon or excitation by an electron. As noted by Greenberg (1973), photodesorption yields of $Y_{pd} \sim 10^{-6}$–10^{-7} are found for physically adsorbed molecules which have no allowed absorption transitions in the gaseous state in the irradiation wavelength range 2000–2750 Å. CS_2, which absorbs in the gaseous state for $\lambda < 2200$ Å, gave the highest yield of $Y_{pd} \sim 10^{-5}$. It is thus expected that photodesorption yields of physically adsorbed molecules will be much higher for $\lambda < 2000$ Å, where strong absorption occurs in the gaseous states of the various molecules. From order of magnitude considerations Greenberg (1973) estimated that Y_{pd} could reach 10^{-2} in spectral regions of high gaseous absorption. The fact that any photodesorption occurs at all in spectral regions with no gaseous absorption can be ascribed to the fact that when a particle is adsorbed its electronic states can be redshifted or blueshifted, depending on the particular surface-adsorbed particle combination.

From the preceding discussion it is expected that in the wavelength region of *strong* molecular photoabsorption, physically adsorbed molecules will have photodesorption cross sections similar to their gas-phase photoabsorption cross sections. Photoabsorption cross sections in the 912–1900 Å region of some molecules which are expected to be astrophysically abundant will be briefly summarized. From Watanabe & Zelikoff (1953), H_2O molecules have a mean photoabsorption cross section $\bar{\sigma}_{pa} \sim 3 \times 10^{-18}\,cm^2$ in the 1200–1850 Å wavelength region and have $\bar{\sigma}_{pa} \sim 10^{-17}\,cm^2$ in the 1000–1200 Å region. CH_4 molecules have a σ_{pa} rising approximately linearly from zero at 1500 Å to $5 \times 10^{-17}\,cm^2$ at 900 Å (Ditchburn 1955), equivalent to $\bar{\sigma}_{pa} \sim 10^{-17}\,cm^2$ for diffuse interstellar photons between 912 and 1900 Å. NH_3 molecules have $\bar{\sigma}_{pa} \sim 4 \times 10^{-18}\,cm^2$ in the 1200–2000 Å region (Watanabe 1954) and $\bar{\sigma}_{pa} \sim 10^{-17}\,cm^2$ in the 900–1200 Å region. H_2CO molecules have $\bar{\sigma}_{pa} \sim 2$–$3 \times 10^{-17}\,cm^2$ in the 900–1200 Å region (Gentieu & Mentall 1970). From the work of Huffman, Larrabee & Tanaka (1964) on the ultraviolet band spectrum of CO, $\bar{\sigma}_{pa} \sim 2$–$3 \times 10^{-17}\,cm^2$ is estimated for the 912–1000 Å region and from Myer & Samson (1970) $\bar{\sigma}_{pa} \sim 3$–$4 \times 10^{-19}\,cm^2$ is estimated for the 1000–1550 Å region; equivalent to $\bar{\sigma}_{pa} \sim 1$–$2 \times 10^{-18}\,cm^2$ for diffuse interstellar photons between 912 and 1900 Å. Thus a reasonable estimate of the mean photoabsorption cross section in this wavelength region for the above molecules is $\bar{\sigma}_{pa} \sim 5 \times 10^{-18}\,cm^2$.

The photodesorption experiments quoted earlier show that for $\lambda > 3500$–4000 Å, photodesorption does not occur, while at shorter wavelengths σ_{pd} increases with decreasing λ, and is still increasing at the various experimental short wavelength cutoffs. The experiment of Fabel *et al.* (1973), which measured a value of σ_{pd} for the shortest wavelength so far (1850 Å), found $\sigma_{pd} = 5.5 \times 10^{-18}\,cm^2$. Guided by these experimental results, by the ultraviolet molecular photoabsorption cross sections estimated above, and by the theoretical work of Gersten *et al.*, I adopt $\bar{\sigma}_{pd} = 5 \times 10^{-18}\,cm^2$ as an average photodesorption cross section over the 912–1900 Å wavelength region, corresponding to $Y_{pd} = 5 \times 10^{-3}$ for each 912–1900 Å photon incident on a monolayer. Photodesorption by photons with longer wavelength can be neglected because of the lower photodesorption cross section and because of the strong absorption of photons by the 2175 Å interstellar extinction feature which sets in at ~ 1900 Å.

Metal atoms adsorbed on surfaces should have a very low photodesorption cross section, due to the very fast penetration of the surface barrier by electrons in such a system (Menzel 1975). If mechanism (iii) is responsible for photodesorption then only molecules can be desorbed in any case. The experimental data on photodesorption pertains to stable molecules with large dissociation energies. Metal hydride molecules, such as might be found trapped on grain surfaces (Paper III), in general have considerably lower dissociation energies. If the metal atom component of a metal hydride molecule has a high mass, or experiences a considerably greater attraction to the surface than the H atom component, then absorption of a photon by the adsorbed metal hydride molecule may lead to dissociation rather than desorption of the molecule.

The question of whether photodesorption of dirty-ice type mantles can occur is now considered. For ordinary solids photodesorption (photosputtering) is not known to occur (for the special case of alkali halide crystals, photosputtering occurs by means of a mechanism peculiar to those materials, *cf.* Townsend & Elliott 1970). It is expected that on most solids photodesorption will be suppressed due to rapid transfer of electronic excitation along lattice bonds (Watson & Salpeter 1972). In addition, mechanism (iii) would tend to be suppressed in a crystal, since a vibrating molecule would not be able to interact with its neighbours because of the stiffness of the lattice bonds. The case of an ice crystal is uncertain since it does not possess covalent or ionic bonding, the crystal being bound by the hydrogen bond (Pauling 1960), which is only slightly stronger than the van der Waals' long-range dispersive forces responsible for physical adsorption. Greenberg (1973) found photodesorption of physically adsorbed H_2O to occur only for surface coverages up to a monolayer, with no photodesorption detected for multilayer H_2O adsorption. Further experiments are desirable for $\lambda < 1850\,Å$, where H_2O exhibits strong absorption in the gaseous state. It would appear, though, that the H bonded crystal structure of ice suppresses the weak photodesorption found for irradiation of H_2O monolayers by photons with $2000 < \lambda < 2750\,Å$, so that photodesorption from pure ice crystals might also be suppressed for $\lambda < 2000\,Å$. However, interstellar ice grains are highly unlikely to accrete pure H_2O mantles. The dirty-ice model of van de Hulst (1949) assumed a mixture of CH_4, NH_3, H_2O and other hydrides, in proportions according to the cosmic abundances of C, N and O, etc. Recent observational work on interstellar molecules indicates that CO molecules and various other more complex molecules are likely to be abundant in a dirty-ice mantle as well (*cf.* Duley 1974). Hunter & Donn (1971) found that on depositing a mixture of NH_3–H_2O or CH_4–H_2O on a surface substrate no mixed hydrogen bonded species were detected, with hydrogen bonding occurring only for clusters of NH_3 or clusters of H_2O. Their results indicate that only van der Waals attraction occurred between different molecular species, with a typical binding energy per molecule of $\sim 0.1\,\mathrm{eV}$ (*cf.* Watson & Salpeter 1972). Clusters of H_2O molecules would not be expected to occur in a dirty-ice mantle, due to the random nature of their accretion, and the various other molecular species intermixed in the mantle would suppress any incipient hydrogen bonding. Thus a freshly accreted dirty-ice mantle should be bound only by multilayer physical adsorption and should exhibit photodesorption properties identical to those of a monolayer of physically adsorbed molecules. I therefore adopt a photodesorption cross section, for molecules which are part of a mantle, of $\bar{\sigma}_{\mathrm{pd}} = 5 \times 10^{-18}\,\mathrm{cm}^2$, equivalent to a yield $Y_{\mathrm{pd}} = 5 \times 10^{-3}$ for each incident photon with $912 < \lambda < 1900\,Å$.

If mechanism (iii) is responsible for photodesorption, then it might also be expected that absorption of infrared photons by purely vibrational transitions would also lead to photodesorption (Watson & Salpeter 1972). However, even if the probability of desorption of a molecule after absorption of an infrared photon is the same as after absorption of an ultraviolet photon, Watson & Salpeter show that infrared photodesorption is unlikely to be important since vibrational oscillator strengths are typically $\approx 10^{-5}$ those of electronic transitions, whereas the diffuse infrared photon flux in the wavelength region of interest is only $\approx 10^2$ times that estimated below for ultraviolet photons capable of photodesorption. Thus, in unobscured regions of interstellar space the infrared photodesorption rate will be $\sim 10^{-3}$ that for ultraviolet photodesorption and even in shielded dense clouds ultraviolet photodesorption will always be the controlling factor in mantle growth.

In order to explain the general absence in interstellar space of the 3.1 μm water-ice absorption feature it has been proposed (Donn & Jackson 1970) that irradiation of freshly accreted ice mantles by ultraviolet photons (again with $\lambda < 2000$ Å) will convert the molecules in the mantles into more complex species. Such an effect might lead to a less volatile mantle, with stronger lattice bonding if radicals are present (Donn & Jackson 1970). Greenberg & Yencha (1973) have irradiated a 'cosmic abundance' mixture of H_2O, CH_4 (or C_2H_6) and NH_3, (20 mg total weight) with photons in the wavelength range 1400–2000 Å. They found that the measured rate of conversion of these simple molecules to more complex organic molecules implied a photon efficiency of ~ 0.05–0.1 per cent, i.e. $\lesssim 10^{-3}$ molecules were converted per incident photon. The estimate above of $Y_{\rm pd} \geqslant 5 \times 10^{-3}$ for this wavelength range implies that, once exposed to ultraviolet photons, mantles will be destroyed by photodesorption before they can be converted into less volatile material.

The lifetime, $\tau_{\rm pd}$, of an ice grain of radius a against destruction by photodesorption in an unobscured region of interstellar space is given by

$$\tau_{\rm pd} = \frac{4a\rho_{\rm g}}{G_0 Y_{\rm pd} m_{\rm s}}$$

where $\rho_{\rm g} = 1\ {\rm g\,cm^{-3}}$ is the mass density of the grain, $m_{\rm s}$ is the mean mass of a mantle molecule and G_0 is the integrated diffuse interstellar photon flux between 912 and 1900 Å. To obtain G_0 the 930–1125 Å radiation field calculated by Jura (1974) for the solar vicinity has been extrapolated to join with the radiation field longward of 1330 Å derived by Witt & Johnson (1973), yielding $G_0 = 1.7 \times 10^8\ {\rm cm^{-2}/s}$. Thus for $a = 10^{-5}$ cm it is found that $\tau_{\rm pd} = 5 \times 10^4$ yr. A general discussion of the role of photodesorption in destroying ice mantles will be postponed until Paper III, where the conditions for mantle growth are first discussed.

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