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H_2 RECOMBINATION ON INTERSTELLAR GRAINS

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ABSTRACT

From a consideration of relevant theoretical and experimental data it is concluded that H atoms (but not H_2 molecules) will be chemisorbed on interstellar graphite grains, with H_2 formation proceeding efficiently for graphite grain temperatures less than 70 K. It is argued that graphite grains will act as the principal sites for H_2 formation, with a formation rate of $R \approx 4 \times 10^{-17}$ cm^3 s^{-1}. Heating by H_2 molecules formed by surface recombination is analyzed in the context of the available experimental data, and a heating rate is derived and compared with other suggested cloud heating mechanisms. We conclude that H_2 recombination will provide the largest heat source in diffuse clouds if the albedo of interstellar dust in the 912–1200 Å region is high ($\sim$0.9), whereas if the albedo in this wavelength region is lower ($\sim$0.5), photoelectron ejection from grains will tend to predominate, and can explain observed cloud temperatures with a carbon depletion factor of approximately 2, a factor attributable to a normal interstellar abundance of graphite grains.

Subject headings: atomic processes — interstellar: matter

I. INTRODUCTION

Desorption of molecular hydrogen from grain surfaces may provide an important heat source for interstellar clouds. The role of newly formed H_2 molecules as an interstellar heat source has recently been considered by Barlow and Silk (1973), Spitzer and Cochran (1973), and Glassgold and Langer (1974). In this paper we analyze this process with the help of the experimental data available. In § II*a* we consider the nature of the adsorption potential felt by H atoms adsorbed on various grain materials. In § II*b* we consider the actual mechanism involved in the recombination of H atoms chemisorbed on graphite. In § III we derive the heating rate due to H_2 recombination on graphite grains and compare it with other suggested cloud heating mechanisms for a range of model cloud parameters, covering densities from $n = 10$ cm^{-3} up to $n = 10^3$ cm^{-3}.

II. GRAIN SURFACE PROCESSES

a) *The Nature of the Adsorption Potential*

Hollenbach and Salpeter (1971) have derived relationships governing the formation of molecular hydrogen on grain surfaces as a function of the H atom adsorption energy for a range of theoretically possible situations (physical adsorption, enhanced binding sites, semi-chemisorption). We here consider the nature and magnitude of this adsorption potential for a range of likely real grain materials.

In considering the sticking and adsorption of H atoms on interstellar grains it has normally been assumed that only physical adsorption (due to long-range molecular interaction forces) is of importance and that chemical adsorption (due to covalent binding) could be ignored for various reasons which are reconsidered below. However, one of the components of the interstellar grain mixture is believed to be graphite, and there is strong theoretical and experimental evidence for chemisorption of H atoms (but not of H_2 molecules) on graphite surfaces. Quantum-mechanical calculations by Bennett, McCarroll, and Messmer (1971*a*, *b*) using two independent methods (extended Hückel theory or EHT; and complete neglect of differential overlap or CNDO) have predicted in detail that H atoms will be chemisorbed on graphite. The EHT calculations show that for H atoms there will be two types of binding sites on the graphite basal plane: one directly above a lattice carbon atom, with a binding energy $E_{\rm ads}$(H) of 1.14 eV, and the other at a point midway above two adjacent carbon atoms on the hexagonal lattice perimeters, with a binding energy of 1.05 eV. There is no stable binding site above the centers of the hexagonal lattice cells. The CNDO calculations, when scaled according to the ratio of the calculated binding energy and the measured binding energy (7.35 eV) of a lattice carbon atom, give results in agreement with the EHT results. The results of Bennett, McCarroll, and Messmer (1971*a*, *b*) imply that *molecular* hydrogen will not be chemisorbed on graphite, since in order for an unreactive molecule such as H_2 to be chemisorbed on a surface it must first

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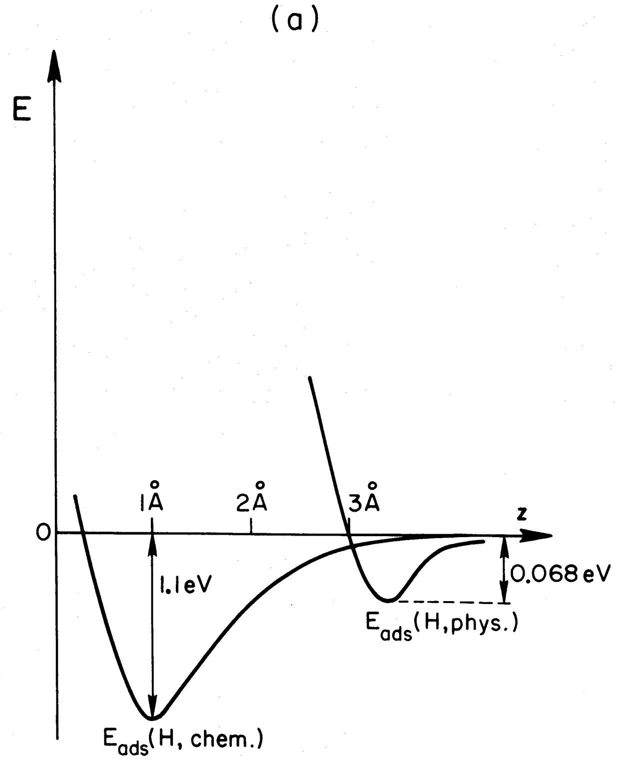

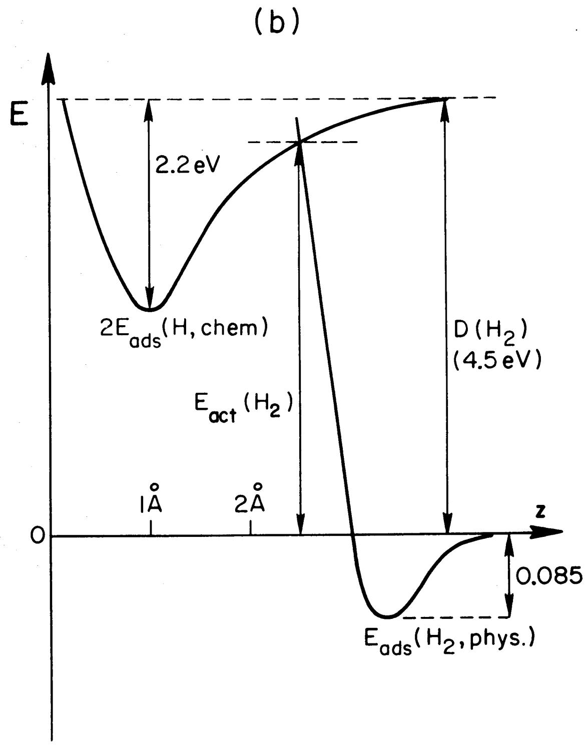

FIG. 1*a*.—Schematic illustration (not to scale) of the potential energy diagram for atomic H adsorbed on graphite. Energy *E* is plotted against the height *Z* of the H atom above the basal plane. E_{ads}(H, phys.) is the potential energy curve for a physically adsorbed H atom. The maximum depth of this curve (0.068 eV) is that inferred by Lee (1975), and the equilibrium height above the plane (3.34 Å) and the height at which the interaction becomes repulsive (3 Å) are assumed to be the same as found for molecular H_2 by Ross and Olivier (1964). E_{ads}(H, chem.), the chemisorption potential curve for atomic H on graphite, is based on that of Bennett *et al.* (1971*b*), with a maximum depth of 1.1 eV taken from Bennett *et al.* (1971*a*). There is no activation energy for chemisorption of atomic H since E_{ads}(H, chem.) intersects E_{ads}(H, phys.) below the $E = 0$ level. The actual total adsorption potential curve is the composite of E_{ads}(H, phys.) and E_{ads}(H, chem.).

FIG. 1*b*.—Schematic illustration (not to scale) of the potential energy diagram for molecular H_2 adsorbed on graphite. The maximum depth of E_{ads}(H_2, phys.), the potential energy curve for physically adsorbed H_2, is taken from Lee (1975). For chemisorption of H_2 to occur, it must first be dissociated into its constituent H atoms. Therefore the zero energy level of chemisorbed H_2 (i.e., two H atoms) lies 4.5 eV [$=$D(H_2)] above the zero energy level of physically adsorbed H_2. $2E_{ads}$(H, chem.) is the composite chemisorption potential energy curve for two H atoms after dissociation of the parent H_2 molecule. E_{act}(H_2), the activation energy for dissociative chemisorprtion of H_2 on the basal plane of graphite, is thus greater than [D(H_2) $-$ $2E_{ads}$(H, chem.)] $\approx$ 2.3 eV.

be broken into its constituent atoms. This can only happen if the sum of the chemisorption binding energies of the individual constituent atoms of the molecule is greater than the dissociation energy *D* of the molecule; i.e., $2E_{ads}$(H) must be greater than $D(H_2)$ (for a detailed discussion see Wise and Wood 1967). For the basal plane of graphite $2E_{ads}(H) = 2.2$ eV, and with $D(H_2) =$ 4.48 eV chemisorption of H_2 can only occur endothermically with an energy input to the system of at least 2.3 eV (see Fig. 1*b*). This is in agreement with laboratory measurements (Lee 1975) which show that H_2 is physically adsorbed on graphite at low temperatures, with a binding energy of 0.085 eV. Unfortunately the magnitude of E_{ads}(H) cannot be directly measured experimentally for graphite, due to rapid surface migration and recombination (McCarroll and McKee 1971). However, direct experimental verification that H atoms undergo chemisorption or graphite can be obtained by other methods. (1) Nikitina, Brants, and Kiselev (1968) have investigated the adsorption of atomic and molecular hydrogen on a graphite surface using electron spin resonance spectroscopy. They find that on adsorption of H_2 molecules the ESR spectrum of the underlying graphite is unchanged, whereas on adsorption of H atoms an extra peak appears in the spectrum, indicating a chemical bond between the surface and the adsorbed H atoms. (2) Beitel (1969, 1972) has measured the sticking probabilities of H and H_2 on graphite, where in this case the sticking probability measured was the probability that the impinging particle was not only adsorbed but remained on the surface for the duration of the experiment, and was thus less than the true sticking probability. For H atoms a sticking probability of 0.038 was found, whereas the sticking probability found for H_2 molecules was less than 10^{-8} (both were measured over the temperature range 360–570 K). This enormous difference cannot be understood if H atoms were only physically adsorbed, since the physical adsorption energy of H should be about 80 percent of that of H_2, which, coupled with the lower mass of the atom, would lead to a lower sticking probability than for the molecule (Hollenbach and Salpeter 1970). The difference in the sticking probabilities can be easily explained, however, if atomic hydrogen were chemisorbed with a binding energy over 10 times larger than that for H_2 (the residence time depends exponentially on the adsorption energy). (3) King and Wise (1963) have measured an activation energy of 0.10 eV for the recombination of H atoms on graphite; and although this was interpreted at the time as an activation energy for reaction between an adsorbed H atom and a directly impinging gaseous H atom, we note that their value is in good agreement with the theoretical prediction from Bennett, McCarroll, and Messmer (1971*a*, *b*) of a surface migration activation energy of 0.09 eV for chemisorbed H atoms. (4) The CNDO calculations of Bennett, McCarroll, and Messmer (1971*b*) also predicted that other atoms besides hydrogen would be chemisorbed on graphite. For O atoms, a much larger activation energy for surface migration was predicted (0.7 eV). Surface recombination of O atoms will thus be inhibited, enabling direct observation of chemisorbed oxygen atoms to be made, as has been done by Barber, Evans, and Thomas (1973) using X-ray induced photoelectron spectroscopy. Further, a binding energy of 4.2 eV for O atoms on graphite can be derived from the work of Datsiev and Belyakov (1968), which should be compared with the scaled prediction from Bennett, McCarroll, and Messmer (1971*b*) of 3.8 eV. We conclude that the theoretical predictions of Bennett *et al.* are supported by all the available experimental evidence and that H atoms will be chemisorbed on graphite with a binding energy, $E_{\text{ads}}(\text{H})$, of 1.1 eV.

Turning to the astrophysical applications, it has sometimes been argued that chemisorption on interstellar graphite grains will be unimportant because either (*a*) there will be a large activation energy to be overcome before chemisorption can occur (Brecher and Arrhenius 1971), (*b*) only a small fraction of surface sites will be chemisorptive (Williams 1968), or (*c*) adsorbed atoms will "plug" chemisorption sites, rendering them inactive (Hollenbach and Salpeter 1971). We consider each of these points in turn.

(*a*) There is in fact no activation energy for the chemisorption of *atoms* on chemisorptive surfaces, in contrast to the case for molecules. For molecules, the occurrence of an activation energy barrier is due to the combined atomic chemisorptive potential curve crossing the molecular physical adsorption potential curve *above* the molecular $E = 0$ potential level (see Fig. 1*b*). For single atoms, the chemisorptive potential curve asymptotically approaches the $E = 0$ level with increasing height of the atom above the surface, never becoming positive (see Fig. 1*a*). Chemisorption of H atoms on graphite grains can therefore take place for any grain or gas temperature with zero activation energy.

b) Chemisorption can take place at any graphite surface site since for the semimetal graphite all of the valence electrons are available for bond formation (Bennett, McCarroll, and Messmer 1971*a*, *b*), rather than just the conduction band electrons as stated by Williams (1968).

c) While not ruling out the possibility of chemisorption on grains, Hollenbach and Salpeter (1971) ignored this possibility on the grounds that incoming atoms would "plug" the chemisorption sites, leaving physical adsorption to occur on top of the then inert sites. However, as noted in the extensive discussion by Bennett, McCarroll, and Messmer (1971*b*), chemisorbed atoms are in fact extremely reactive due to the fact that they have unused valence bonds. They found the effective numbers of bonds for C, N, O, and F atoms chemisorbed on graphite to be ~3.3, 2.4, 1.5, and 0.85, respectively—less in each case than the respective valences. For the case of H atoms the number of effective bonds was found to be ~1.0. However, these are not normal covalent bonds since the lattice carbon atoms are not free atoms (a "normal" covalent bond involves the sharing of one electron between two atoms). For instance, for the case of an adsorbed H atom the bond was found to be made up of equal contributions from *two* basal plane carbon atoms, with the 0.5 bonds per carbon atom due to contributions from the $2s$, $2p_y$, and $2p_z$ electrons. Thus the bond between an adsorbed atom and the surface is dynamic and not localized, enabling recombination to take place with other adsorbed atoms, whose more normal valence bonds are more attractive (the atomic shells having greater overlap) than those of the surface. McCarroll and McKee (1971) concluded that the only process limiting recombination of chemisorbed H atoms on graphite would be surface diffusion, which they assume to take place by quantum-mechanical tunneling. The activation energy of 0.10 eV measured by King and Wise (1963) for H_2 recombination on graphite implies thermal diffusion, as expected in their experimental temperature range of 365–500 K. The magnitude of the measured activation energy implies efficient H_2 formation through thermal effects alone at typical graphite grain temperature in diffuse clouds (~30 K, Leung 1975). For lower grain temperatures, quantum-mechanical diffusion probably dominates over thermal diffusion (Hollenbach and Salpeter 1970; Watson and Salpeter 1972).

Hollenbach (1969) defines the quantum-mechanical diffusion time for migration between adjacent surface sites, t_{QM}, to be equal to $\nu_0^{-1}e^Q$ with

$$Q = (2/\hbar)(2m\Delta E_m)^{1/2}\Delta x\,,$$

where ν_0 is the frequency of surface vibration of an adsorbed atom, m is the mass of the adsorbed atom, ΔE_m is the activation energy for surface diffusion, and Δx is the distance between adjacent surface sites. For an H atom on a graphite surface, $\nu_0 = 10^{13}\ \text{s}^{-1}$, $\Delta E_m = 0.1$ eV, and $\Delta x = 1.42$ Å, yielding $t_{\text{QM}} = 3.7 \times 10^{-5}$ s. The time for an H atom to scan the entire surface of a grain with N surface sites is $\tau_{\text{QM}} \leq N^2 t_{\text{QM}}$ (Hollenbach and Salpeter 1970), which for

$N = 2.8 \times 10^4$ (corresponding to a grain radius of 1.5×10^{-6} cm) gives $\tau_{QM} \leq 2.9 \times 10^4$ s. The mean time between successive H atoms sticking to the grain is $\tau = [\pi a^2 \langle v \rangle S n_H]^{-1}$, where a is the grain radius, $\langle v \rangle$ is the mean thermal velocity of the gas-phase H atoms, S is the H-atom sticking probability, and n_H is the gas-phase H-atom number density. With $a = 1.5 \times 10^{-6}$ cm, a gas temperature of 70 K, $S = 1$ [using the formula of Hollenbach and Salpeter 1970 with $E_{ads}(H) = 1.1$ eV and $T_{gas} = 70$ K], and $n_H = 10$ cm^{-3}, we obtain $\tau \approx 1.2 \times 10^5$ s. Thus quantum mechanical diffusion should assure a two-atom surface for all grain temperatures.

The chemisorptive sites will thus not be plugged, and upon recombination the adsorbed atom will be free to chemisorb further atoms. Note that there *is* an activation energy for reaction between adsorbed atoms and lattice atoms, since in this case lattice bonds must first be broken before reaction can take place. Bar-Nun (1975) has suggested that H atoms may react effectively with interstellar graphite grains. However, Wood and Wise (1969) have measured an activation energy barrier for this reaction of $E_{react} = 0.24$ eV ($E_{react}/k = 2800$ K). The mean time for a chemisorbed H atom to react with a lattice carbon atom will thus be $1/\nu_0 \exp(-2800/T_g)$ seconds, where ν_0 is the frequency of surface vibration of an adsorbed H atom and T_g is the surface temperature. Therefore the relative probability of recombination, compared with reaction with the surface, for H atoms on graphite is given by $P_{recomb}/P_{react} = \pi a^2 \langle v \rangle S n_H / \nu_0 \exp(-2800/T_g)$.

Using the same parameters as above and taking $T_g = 33$ K we find

$$P_{recomb}/P_{react} \approx 7 \times 10^{17}\, n_H\,,$$

whereas for $T_g = 78$ K, $P_{recomb}/P_{react} = 3.3 \times 10^{-4}\, n_H$. It is therefore found that surface reactions between H atoms and graphite grains are not competitive with H_2 recombination for grain temperatures $\leqslant 70$ K. Thus for normal interstellar conditions, with graphite grain temperatures $\leqslant 33$ K (Leung 1975), no significant reaction between H atoms and lattice atoms will occur, although in certain specific situations, where hotter graphite grains can occur, surface reactions may be important (cf. Barlow 1975; Barlow and Silk 1976).

If iron grains exist in interstellar space, then H atoms will be chemisorbed on their surfaces, as has been pointed out by Brecher and Arrhenius (1971). From Wise and Wood (1967), $E_{ads}(H)$ will be 2.95 eV for iron. The semiconductor silicon carbide may be a component of the interstellar grain mixture (Gilra 1971). A chemisorptive binding energy of ~ 1 eV has been measured for silicon carbide at room temperature by Lavrenko, Vasil'ev, and Rokhlenko (1971), but it is uncertain whether all surface sites will be chemisorptive, due to the scarcity of free electrons or holes, believed to be the bond agents for semiconductors (Somorjai 1972). Chemisorption of H atoms will not occur on insulators such as silicates or ice since there are no free electrons or holes available for bond formation. This is in accord with the adsorption energy of 0.065 eV [$E_{ads}(H)/k = 750$ K] measured for H atoms on silica at 78 K by Wood and Wise (1962). A similar value of $E_{ads}(H)$ should apply to silicates.

Hollenbach and Salpeter (1971) have defined a critical grain temperature, T_g(crit), above which H_2 formation will not take place, due to thermal desorption of the H atoms. They derive

$$T_g(\text{crit}) = [E_{ads}(H)/k]/\ln(\nu_0/S\langle v \rangle n_H \pi a^2)\,.$$

For silicates with $E_{ads}(H)/k = 750$ K, $\nu_0 \approx 10^{12}$ s^{-1}, $s\langle v \rangle = 5 \times 10^4$ cm s^{-1} (appropriate for physical adsorption; Day 1973), $a = 5 \times 10^{-6}$ cm, and $n = 10$ cm^{-2} we find T_g(crit) = 19.7 K. For ice grains we take $E_{ads}(H)/k = 690$ K (Lee 1975) and $a = 1 \times 10^{-5}$ cm, and with the other parameters unchanged obtain T_g(crit) = 18.8 K. For graphite grains with $E_{ads}(H)/k = 1.28 \times 10^4$ K, $\nu_0 = 10^{13}$ s^{-1}, $S = 1$, and $a = 1.5 \times 10^{-6}$ cm, we obtain T_g(crit) = 306 K [iron grains with $E_{ads}/k = 3.4 \times 10^4$ K and $a = 5 \times 10^{-6}$ cm would have T_g(crit) = 870 K]. The very high value of T_g(crit) for graphite grains means that H_2 formation can take place over a wide range of physical conditions in interstellar environments.

The dominant role of H_2 formation by chemisorbed atoms on graphite grains can also be inferred from the following considerations. Far-infrared background radiation observations (Pipher 1973) and theoretical computations (Leung 1975) indicate that typical grain temperatures are ~ 16 K for silicate and ice particles, and ~ 33 K for graphite particles, exceeding the value of T_g(crit) appropriate for purely physical adsorption in the case of graphite (~ 19 K from the physisorption energy of Lee 1975). Moreover, grain temperature fluctuations such as those found by Duley (1973) and Greenberg and Hong (1974) will not inhibit molecule formation by *chemisorbed* atoms on graphite grains, contrary to the case for physically adsorbing grains. Since it is found (Barlow 1975), for a grain model based on that of Gilra (1971), that graphite grains contribute over 4 times as much surface area per unit volume of interstellar space as do silicate particles, we shall neglect any contribution to H_2 formation by grains other than graphite.

b) Recombination of Chemisorbed H Atoms

Desorption of H_2 molecules from various metal surfaces following the recombination of chemisorbed H atoms has been investigated experimentally by Van Willigen (1968), Dabiri, Lee, and Stickney (1971), Bradley, Dabiri, and Stickney (1972), Bradley and Stickney (1973), and Balooch *et al.* (1974). In these experiments the angular distribution of newly formed desorbed H_2 molecules was measured, and for certain surface compositions the distribution was found to depart significantly from the expected $\cos\theta$ distribution for thermal desorption, where θ is the angle to the surface normal. The observed nonthermal angular distributions could be described by a $\cos^d\theta$ relation, where d was found to be in the range 2.5–7.0, depending on the surface studied. This $\cos^d\theta$ relation implies the addition of molecular kinetic energy in the normal direction, consistent with the measurement by Dabiri, Lee, and Stickney (1971) of a suprathermal velocity distribution for H_2 molecules desorbed from an uncleaned Ni sample which gave a $\cos^d \theta$ angular distribution.

Goodman (1972) has interpreted the experimental data in terms of a model whereby the recombination energy of the newly formed H_2 molecules becomes available in the form of kinetic energy normal to the surface. If the H_2 recombination energy, $D(H_2)$, is less than the sum of the adsorption energies of the H atoms, $2E_{\text{ads}}(H)$, trapping of the molecule will occur, resulting in thermalization to the surface and eventual thermal ($\cos \theta$) desorption. If on the other hand $D(H_2) > 2E_{\text{ads}}(H)$, then nonthermal ($\cos^d \theta$, $d > 1$) desorption can occur, the magnitude of d being proportional to the excess of the recombination energy over the adsorption energies. Since surface adsorption energies depend on the surface chemical composition, this is consistent with the results of Bradley, Dabiri, and Stickney (1972), who found that d depended critically on the chemical contamination of particular surfaces being studied.

An alternative model for the interpretation of the experimental results was proposed by Van Willigen (1968) and has been modified by Bradley and Stickney (1973). In this model there exists a potential barrier E_m against surface migration of H atoms, which must be overcome before recombination can occur. An unstated assumption implicit in the Bradley and Stickney model is that all of the H_2 recombination energy goes toward overcoming the chemisorption energies of the two H atoms, leaving the remaining difference ΔE_{ads} [$=2E_{\text{ads}}(H) - D(H_2)$] to be overcome by the surface migration energy E_m. If $E_m > \Delta E_{\text{ads}}$, a nonthermal distribution results. The model is, however, susceptible to experimental verification, since an exponential dependence upon surface temperature is predicted for the angular distribution of the desorbed molecules. However, a dependence upon surface temperature is definitely *not* seen, as noted by Balooch *et al.* (1974). This nondependence on surface temperature arises naturally in the Goodman model, since all that is required for nonthermal desorption is that $D(H_2)$ be greater than $2E_{\text{ads}}(H)$.

Molecular hydrogen was found to be desorbed thermally from the *clean* surfaces of Ni, Fe, Pt, and Nb; and Table 1 of Wise and Wood (1967) shows that for all these metals $2E_{\text{ads}}(H) > D(H_2)$. Clean Cu, on the other hand, for which nonthermal desorption of H_2 was found, is known to exhibit radically different chemisorptive behavior to that of the other metals (Pritchard 1972). Ostrovskii (1967) has found that only 10 percent of the surface of Cu will dissociatively chemisorb H_2. It would appear that this 10 percent of the surface provides the H atom source in the experiments and that migration and recombination on the 90 percent of the surface which is less strongly adsorbing [$2E_{\text{ads}}(H) < D(H_2)$] leads to the observed nonthermal desorption. Other arguments against the Van Willigen type of model can be found in Goodman (1972). All of the experimental results on H_2 desorption are consistent with Goodman's model; and since the theory is directly applicable to the case of H atoms chemisorbed on graphite, it will be adopted in what follows.

Consider two H atoms, designated by subscripts 1 and 2, migrating on a grain surface. Before recombination the total energy ϵ of the system is given by

$$\epsilon = V_1 + V_2 + E_2 - 2E_{\text{ads}}(H) , \qquad (1)$$

where atoms 1 and 2 are vibrating with energies V_1 and V_2 with respect to the surface, and E_2 is the translational energy (tangential to the surface) of atom 2 (atom 1 is taken to be at rest).

After recombination the total energy of the system will be given by

$$\epsilon = I_m + E_{tm} + E_{nm} - D(H_2) . \qquad (2)$$

Here I_m is the internal (vibrational and rotational) energy of the newly formed molecule, E_{tm} is the translational energy of the molecule tangential to the surface, and E_{nm} is the translational energy normal to the surface.

Conservation of tangential momentum (see Goodman 1972) gives $E_{tm} = \frac{1}{2}E_2$, and on equating (1) and (2) we therefore obtain

$$E_R \equiv I_m + E_{nm} = D(H_2) - 2E_{\text{ads}}(H) + (9/2)kT_g , \qquad (3)$$

where T_g is the grain temperature. Here E_R is the total energy available to the molecule for sharing between internal energy and kinetic energy *normal* to the surface. For $T_g \approx 33$ K the last term in equation (3) can be neglected, so with $D(H_2) = 4.48$ eV and $E_{\text{ads}}(H) = 1.1$ eV we find that $E_R = 2.3$ eV. The preceding analysis ignores the possibility that a significant amount of the molecular recombination energy may be removed by the grain, through phonon or electron tunneling de-excitation processes, thereby preventing desorption. These two processes have been considered by Williams (1968). Phonon de-excitation is shown to be unimportant, as is electron de-excitation for physical adsorption 3 Å above the graphite plane, making stabilization of a newly formed H_2 quasi-molecule difficult. However, for the case considered here the chemisorbed H atoms will be 1 Å above the graphite surface, where the density of electrons is much increased, so that stabilizing rotational de-excitation collisions can take place efficiently, although vibrational de-excitation will still be inefficient. Another possible process for the removal of molecular energy is through collisions with adjacent adsorbed molecules. This could only be effective at high cloud densities where a significant fraction of a H_2 monolayer was adsorbed on a grain. The experimental work by Marenco *et al.* (1971), on the adsorption and recombination of H atoms on the surface of a Ge bolometer, provides some evidence for (a small) energy transfer to the surface in the presence of an adsorbed monolayer of H_2 molecules. However, it is also found that the adsorbed H_2 monolayer is removed by the recombining H atoms, so that the net effect of H_2 molecule formation appears to be either conversion of the recombination energy into translational energy of the newly formed molecule or, in some cases, transferral to translational energy of an adjacent adsorbed particle. In what follows, the latter case may be considered equivalent to the former for the purposes of determining the resultant cloud heating rate.

The mechanism by which recombination energy is converted into molecular translational energy normal to the surface must now be considered. In deriving their estimate of the amount of energy converted into molecular translational energy, Hollenbach and Salpeter (1970) treated the process as two physically adsorbed H atoms interacting separately with surface atoms. However, once H atoms enter their mutual chemical potential well, they form a quasi-bound system, which should be treated as a composite particle from which energy may only be removed in quantum amounts. The exact process through which the molecule converts its internal energy into translational energy must be considered uncertain at present. For instance, Willis and Fitton (1975) have suggested that electron correlation effects may be important on graphite surfaces, but the following model is proposed here: Recombination is expected to be to the uppermost vibrational level of the ground electronic state, e.g., to the quasi-bound $V = 14, J = 5$ state in analogy to the case of thermolecular recombination (Roberts, Bernstein, and Curtiss 1968). From this state stabilization takes place by means of a $\Delta J = -2$ rotational de-excitation transition (Roberts, Bernstein, and Curtiss 1968; Williams 1968). The molecule can then interact with surface atoms, converting internal vibrational energy into kinetic energy into kinetic energy away from the grain, in a manner rather like the interaction of a compressed spring with a desk surface. When an H_2 molecule, vibrating at a frequency $\sim 10^{15}\ \mathrm{s}^{-1}$ and oscillating in the surface potential, collides with a surface atom (in effect a repulsive potential), the surface atom cannot respond fast enough to absorb the vibrational energy (the maximum phonon frequencies being $\lesssim 10^{13}\ \mathrm{s}^{-1}$), and so behaves essentially as a rigid body. The molecule will rebound, and the amount of energy transferred from vibrational to kinetic energy depends on the amplitude of the molecule at the moment of impact. The maximum amplitude of the newly formed vibrationally excited molecule will be 3.5 Å (Roberts, Bernstein, and Curtiss 1968). Since the recombining atoms are situated only 1 Å above the graphite plane, either directly above a lattice atom or above the midpoint between two lattice atoms 1.4 Å apart, the probability of collision will be extremely high, with practically all the vibrational energy being transferred into translational energy during the rebound. This would be in agreement with the results of Goodman (1972) which show that practically all of the available recombination energy must be converted into translational energy for the cases where H_2 is found to be nonthermally desorbed. On leaving the surface of a graphite grain, after overcoming the combined potential felt by the two H atoms, a newly formed H_2 molecule would therefore have a kinetic energy of $E_{\mathrm{rec}}' = 2.3$ eV.

Ultraviolet dissociation of H_2 molecules leads to an additional heat source, amounting to ~ 0.5 eV per dissociation (Stephens and Dalgarno 1973; Milgrom, Panagia, and Salpeter 1973). Since, in equilibrium dissociations balance recombinations, we can regard this energy source as a correction to E_{rec}' to give $E_{\mathrm{rec}} = 2.8$ eV. Vibrational de-excitation of H_2 molecules in clouds can provide another small additional heat source, amounting, however, to only $\sim 10^{-6}\, n$ eV per H_2 molecule formed in a cloud of density n particles cm^{-3} (Stecher and Williams 1973; Silk 1973), and is neglected here.

c) *Photodesorption*

Consideration of the available experimental and theoretical data on photodesorption (Barlow 1975) leads to an estimate for an average yield Y (number of adsorbed particles desorbed per incident photon) for photons with $912 \leq \lambda \leq 1900$ Å incident on a monolayer, of $Y \approx 5 \times 10^{-3}$. This corresponds to a photodesorption cross section of $\sigma_{\mathrm{pd}} = 5 \times 10^{-18}\ \mathrm{cm}^2$ per adsorbed particle. Watson and Salpeter (1972) have shown that this sort of yield (or even a yield of unity) would not affect H_2 recombination on grain surfaces. Although adsorbed H atoms will be removed by recombination, the possibility exists that photodesorption of adsorbed H_2 molecules may provide a heat input to clouds, through a mechanism similar to that described for H_2 recombination. However, we find that, even if a monolayer of H_2 molecules were adsorbed on grain surfaces, the heat input to the gas (assuming $Y = 5 \times 10^{-3}$ and an energy of 2.2 eV per desorbed H_2 molecule) is smaller than that due to the other principal heating mechanisms considered here. It may be difficult for a monolayer of H_2 molecules to form on grains in diffuse interstellar clouds—the maximum grain temperature for this to occur is typically 15–19 K (Lee 1975). More importantly, experimental work by Ryabchuk *et al.* (1974) has shown that NO molecules, photodesorbed from an Al_2O_3 surface by photons with $1850\ Å \leq \lambda \leq 2300$ Å, have no excess kinetic energy over that expected for thermal desorption from the surface, in contrast to the experimental situation for H_2 recombination discussed in the previous section. For these reasons we ignore photodesorption as a heat source in interstellar clouds.

III. APPLICATION TO INTERSTELLAR CLOUDS

a) *Heating by* H_2 *Recombinations*

Molecules ejected from grain surfaces will rapidly share their kinetic energy with other particles through collisions. The characteristic time scale for this to occur is $10^{10}/n$ s, where n is the ambient gas particle density.

The heating rate Γ_{rec} associated with surface recombination of H atoms in an interstellar cloud of density

$n \equiv n_{\mathrm{H\,I}} + 2n_{\mathrm{H_2}}$ ($n_{\mathrm{H\,I}}$ and $n_{\mathrm{H_2}}$ denote the densities of atomic and molecular hydrogen) is given by

$$\Gamma_{\mathrm{rec}} = Rn^2(1-f)E_{\mathrm{rec}}\,,$$

where $f \equiv 2n_{\mathrm{H_2}}/n$ and R is the H_2 formation rate constant. R is given by (Hollenbach, Werner, and Salpeter 1971, hereafter HWS)

$$R = \tfrac{1}{2}S\langle v\rangle n_g\sigma_g n^{-1}\,,$$

where $n_g\sigma_g$ is the product of the dust grain number density and mean geometric cross section for those grains on which H_2 recombination can take place. As discussed in § II*a*, and below, we assume that only graphite grains give a significant contribution to H_2 formation.

If the 2175 Å peak of the interstellar extinction curve is ascribed to graphite grains of radius $\sim 1.5 \times 10^{-6}$ cm (Gilra 1971), then Savage's (1975) estimate for the strength of this feature, together with the graphite grain extinction efficiencies of Wickramasinghe, Lukes, and Dempsey (1974), yields $n_g\sigma_g = 6.1 \pm 0.8 \times 10^{-22}\,n\ \mathrm{cm}^{-1}$ (Barlow 1975), leading to an estimate for the H_2 formation rate of $R = (3.7 \pm 0.5) \times 10^{-17}\ \mathrm{cm^3\,s^{-1}}$ for $S = 1$ and $\langle v\rangle = 1.2 \times 10^5\ \mathrm{cm\,s^{-1}}$. The nominal error estimate is ascribed to uncertainty in the mean interstellar value of $N_{\mathrm{H}}/A_v \approx 2 \times 10^{21}\ \mathrm{cm^{-2}\,mag^{-1}}$ (Bohlin 1974; Jenkins and Savage 1974; Gorenstein 1975; Ryter, Cesarsky, and Audouze 1975).

This estimate implies that approximately 40 percent of the cosmic abundance of carbon will be tied up in such grains. The contribution to R by graphite is also in agreement with Jura's (1975) estimate for R, based on *Copernicus* OAO observations of H_2.

With $R = 3.7 \times 10^{-17}\ \mathrm{cm^3\,s^{-1}}$ and $E_{\mathrm{rec}} = 2.8$ eV, we find

$$\Gamma_{\mathrm{rec}} = 1.65 \times 10^{-28}n^2(1-f)\ \mathrm{ergs\,cm^{-3}\,s^{-1}}\,.$$

We shall see in § III*c* that for $(1-f) \ll 1$ the heating rate Γ_{rec} becomes independent of the value assumed for R.

b) *Other Heating Mechanisms*

For the purpose of comparison with the heating rate due to H_2 recombination, we include some other suggested cloud heating mechanisms in our model cloud calculations.

Watson (1972) has proposed that photoelectron ejection from grains could provide a significant heat source, with a heating rate Γ_{pe} given by

$$\Gamma_{\mathrm{pe}} = G_{\mathrm{pe}}Y_{\mathrm{pe}}E_{\mathrm{pe}}n_g\langle\sigma\rangle_{\mathrm{pe}}{}^{\mathrm{abs}}\exp(-\tau_{\mathrm{uv}})\,,$$

where G_{pe} is the free space ultraviolet photon flux in the wavelength interval 912–1230 Å. We adopt a flux identical to that of Watson (1972), equivalent to $G_{\mathrm{pe}} = 3.8 \times 10^7\ \mathrm{cm^{-2}\,s^{-1}}$. Y_{pe} is the photoelectron yield. We assume graphite and silicates to be the most important grain species for this mechanism and take a value of 4.5 for the ratio of graphite to silicate cross sections per unit volume of interstellar space. From Feuerbacher and Fitton (1972) we take average yields, for the 10–13.6 eV region, of 0.025 for graphite and 0.3 for silicates (after multiplication by a factor of 2.5 to allow for small size effects as recommended by Watson 1972). The weighted average yield for graphite and silicate grains is then $Y_{\mathrm{pe}} = 0.075$. E_{pe}, the average energy of an ejected photoelectron, is taken to be 1.75 eV, with grain charging ignored. The quantity $n_g\langle\sigma\rangle_{\mathrm{pe}}{}^{\mathrm{abs}}$ is the mean grain absorption cross section for 10–13.6 eV photons, and τ_{uv} is the optical depth for penetration of these photons into a cloud. Unfortunately both these quantities depend critically on the dust albedo in the 912–1230 Å region, a quantity not definitely known at present. HWS assumed a dust albedo of ~ 0.5, giving $\tau_{\mathrm{uv}} \sim 2.5\,\tau_v$, where τ_v is the visual extinction optical depth. However, there are indications from the work of Witt and Lillie (1973) and Mezger, Smith, and Churchwell (1974) that the dust albedo may be high in this region. Therefore for our comparison of heating rates we consider two cases. (*a*) an albedo of 0.9, whence, for a mean extinction over the 912–1200 Å region of $4A_v$, leading to $\tau_{\mathrm{uv}} = \tau_v$ from Whitworth (1975), we obtain

$$\Gamma_{\mathrm{pe}} = 1.48 \times 10^{-27}n\exp(-\tau_v)\ \mathrm{ergs\,cm^{-3}\,s^{-1}}\,;$$

(*b*) an albedo of 0.5, whence

$$\Gamma_{\mathrm{pe}} = 7.4 \times 10^{-27}n\exp(-2.5\,\tau_v)\ \mathrm{ergs\,cm^{-3}\,s^{-1}}\,.$$

We also include in our comparison calculations the chemical heating mechanism of Dalgarno and Oppenheimer (1974) with a heating rate

$$\Gamma_{\mathrm{ch}} = 1.5 \times 10^{-29}n^2 f\exp(-\tau_{\mathrm{uv}})\ \mathrm{ergs\,cm^{-3}\,s^{-1}}\,,$$

where we have included a flux attenuation term $\exp(-\tau_{\mathrm{uv}})$. We assume that no heating is produced if C II/C I $\ll 1$, since the heating cycle must be initiated by the reaction $\mathrm{C^+} + \mathrm{H_2} \rightarrow \mathrm{CH_2}^+ + h\nu$.

We assume that any cosmic ray or X-ray heating of interstellar clouds is insignificant (cf. Spitzer and Jenkins 1975).

c) *Evaluation of Cloud Heating Rates and Temperatures*

Tables 1A and 1B display heating rates at the centres of uniform-density clouds covering a range in densities $10 \leq n \leq 10^3\ \mathrm{cm^{-3}}$ for the cases $\tau_{\mathrm{uv}} = \tau_v$ and $\tau_{\mathrm{uv}} = 2.5\,\tau_v$. The density n ($\equiv n_{\mathrm{H\,I}} + 2n_{\mathrm{H_2}}$), mass M, radius r, and visual optical depth to the cloud center τ_v are related by the formulae (cf. HWS):

$$n = (500\,M_\odot/M)^{1/2}\tau_v{}^{3/2} \times 260\ \mathrm{cm^{-3}}\,;$$

$$r = (M/500\,M_\odot)^{1/2}\tau_v{}^{-1/2} \times 2.3\ \mathrm{pc}\,.$$

M, τ_v, and n are tabulated for each cloud, along with $N\,(=N_{\mathrm{H\,I}} + N_{\mathrm{H_2}} = nr)$, the column density of hydrogen nuclei along a radius to the center of the cloud.

The fractional abundance of atomic hydrogen, $(1-f)$, has been calculated utilizing the approach of Jura (1974), valid when H_2 is on the square-root

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TABLE 1A

EVALUATION OF HEATING RATES AND TEMPERATURES AT CLOUD CENTERS FOR $\tau_{uv} = \tau_v$

PARAMETER	$M/M_\odot$ 450	500	500	500	500
τ_v	0.1	0.24	0.53	1.1	2.46
n(cm^{-3})	10	30	100	300	10^3
N(cm^{-2})	2.2×10^{20}	5.3×10^{20}	1.2×10^{21}	2.5×10^{21}	5.5×10^{21}
$(1-f)$	0.94	0.45	7.4×10^{-2}	3.0×10^{-2}	3.0×10^{-2}
Γ_{rec}	1.6×10^{-26}	6.7×10^{-26}	1.2×10^{-25}	4.6×10^{-25}	5.0×10^{-24}
Γ_{pe}	1.3×10^{-26}	3.5×10^{-26}	8.7×10^{-26}	1.5×10^{-25}	1.3×10^{-25}
Γ_{ch}	8.0×10^{-29}	5.8×10^{-27}	8.0×10^{-26}	4.4×10^{-25}	1.3×10^{-24}
C II/C I:					
$\delta = 1.0$	3.1×10^3	880	190	29	$\ll 1$
$\delta = 0.5$	7.4×10^3	2.1×10^3	450	79	1.5
$\delta = 0.2$	2.5×10^4	7.0×10^3	1.4×10^3	230	11
T(K):					
$\delta = 1.0$	27	25	20	17	14
$\delta = 0.5$	36	33	28	23	20
$\delta = 0.2$	60	53	49	38	30

portion of the curve of growth, and therefore applicable to all the clouds considered here. Jura's equation (A5) has been modified to take into account dust attenuation following an $\exp(-\tau_{uv}z)$ opacity law for H_2 dissociating photons. The quantity z is the fractional depth into the cloud, so that $z = 1$ at the center. We obtain

$$\frac{d}{dz}\left[\frac{\beta^2 I^2}{2R^2 n^3 r}\frac{f^2}{(1-f)^2}\exp(-2\tau_{uv}z)\right] = f\,,$$

where $\beta = 4.2 \times 10^5$ cm^{-1}, I is the unattenuated H_2 dissociation rate of $I = 5.4 \times 10^{-11}$ s^{-1}, and $R = 3.7 \times 10^{-17}$ cm^3 s^{-1}. The fractional abundances of molecular hydrogen found here are larger than those predicted by the theory of HWS, but are in good agreement with the detailed numerical calculations for diffuse clouds by Glassgold and Langer (1974). The results are also in qualitative agreement with the concentration of f to very high and very low values observed by Spitzer *et al.* (1973).

For $(1-f) \ll 1$ it is possible to show that

$$(1-f) = (\beta^2 I^2/2R^2 n^3 zr)^{1/2}\exp(-\tau_{uv}z)\,.$$

In this case $(1-f)$ will be proportional to $1/R$. The H_2 recombination heating rate Γ_{rec}, proportional to the product of $(1-f)$ and R, will therefore be independent of the value adopted for R when $(1-f) \ll 1$. Γ_{rec} is, however, directly proportional to the H_2 dissociation rate, $I\exp(-\tau_{uv}z)$, for $(1-f) \ll 1$. Since Γ_{pe} and Γ_{ch} are also directly proportional to the ultraviolet flux, we see that these mechanisms will all scale with the ultraviolet flux in the same manner in a dense cloud exposed to a more intense radiation field, such as that due, for instance, to the proximity of a hot star. We have taken into account residual dissociation of H_2 by the observed cosmic-ray flux ($\zeta_H \sim 10^{-17}$ s^{-1}) by setting $1 - f = 0.03$ (cf. Glassgold and Langer 1974).

The ionization equilibrium of carbon has been computed following the method of Werner (1970). The calculations have been modified to include the

TABLE 1B

EVALUATION OF HEATING RATES AND TEMPERATURES AT CLOUD CENTERS FOR $\tau_{uv} = 2.5\tau_v$

PARAMETER	$M/M_\odot$ 450	500	500	500	500
τ_v	0.1	0.24	0.53	1.1	2.46
n(cm^{-3})	10	30	100	300	10^3
N(cm^{-2})	2.2×10^{20}	5.3×10^{20}	1.2×10^{21}	2.5×10^{21}	5.5×10^{21}
$(1-f)$	0.92	0.33	3.4×10^{-2}	3.0×10^{-2}	3.0×10^{-2}
Γ_{rec}	1.5×10^{-26}	4.9×10^{-26}	5.6×10^{-26}	4.4×10^{-25}	4.9×10^{-24}
Γ_{pe}	5.8×10^{-26}	1.2×10^{-25}	2.0×10^{-25}	1.4×10^{-25}	1.6×10^{-26}
Γ_{ch}	9.3×10^{-29}	5.0×10^{-27}	3.8×10^{-26}	8.6×10^{-26}	...
C II/C I:					
$\delta = 1.0$	3.2×10^3	720	96	25	$\ll 1$
$\delta = 0.5$	9.0×10^3	1.7×10^3	220	66	$\ll 1$
$\delta = 0.2$	4.0×10^4	6.8×10^3	1.7×10^3	200	$\ll 1$
T(K):					
$\delta = 1.0$	39	30	21	15	13
$\delta = 0.5$	60	45	31	20	18
$\delta = 0.2$	150	97	58	32	35

temperature dependence of the carbon recombination coefficient, and to incorporate an unattenuated carbon ionization rate of $2.1 \times 10^{-10}\ \mathrm{s}^{-1}$ (derived from Jura's 1974 solar vicinity radiation field), with dust attenuation over 912–1100 Å corresponding to $\tau_{\mathrm{uv}} = \tau_v$ and $\tau_{\mathrm{uv}} = 2.5\ \tau_v$.

We have considered the effects on our results of carbon depletion by allowing the carbon depletion factors to have values corresponding to: no depletion ($\delta = 1.0$); depletion by a factor of 2 ($\delta = 0.5$); and depletion by a factor of 5 ($\delta = 0.2$). It is argued elsewhere (Barlow 1975) that the main source of carbon depletion in *diffuse* clouds will be that due to the original condensation of carbon into graphite grains in circumstellar environments. Therefore, from the result described in § III*a* that ~40 percent of carbon is in the form of graphite grains, our preferred depletion factor would be $\delta = 0.5$.

Hobbs (1974) has found that for low-density clouds the fractional ionization n_e/n is nearly constant over a range of cloud densities of about 15. If carbon is the main electron source in clouds, then the present results predict $n_e \propto n$ up to $n \sim 300$–$10^3\ \mathrm{cm}^{-3}$.

Cloud kinetic temperatures T have been calculated by setting the total heating rate Γ equal to the cooling rate Λ due to collisional excitations of C II and C I. C I is found to be important only in the $n = 10^3\ \mathrm{cm}^{-3}$ cloud, so for the other clouds

$$\Lambda = 3.7 \times 10^{-4} n^2 \delta \left[(1 - f) L_{\mathrm{H}}(\mathrm{C\,II}/T) + \frac{f}{2} L_{\mathrm{H}_2}(\mathrm{C\,II}/T) + 3.7 \times 10^{-4} \delta L_e(\mathrm{C\,II}/T) \right] .$$

The cooling efficiency for H atom excitation, $L_{\mathrm{H}}(\mathrm{C\,II}/T)$, and electron excitation, $L_e(\mathrm{C\,II}/T)$, are taken from Dalgarno and McCray (1972); and that for H_2 excitation, $L_{\mathrm{H}_2}(\mathrm{C\,II}/T)$, is taken from Chu and Dalgarno (1975). For the $n = 10^3\ \mathrm{cm}^{-3}$ cloud, where cooling by C I is important, $L_{\mathrm{H}}(\mathrm{C\,I}/T)$ is taken from Dalgarno and McCray (1972) and the assumption is made that $L_{\mathrm{H}}/L_{\mathrm{H}_2}$ scales in the same manner for C I and C II. Cooling by CO molecules is neglected for the diffuse clouds considered here.

Inspection of Tables 1A and 1B reveals the following points: for the case of $\tau_{\mathrm{uv}} = \tau_v$, the cloud temperatures decline slowly for a given carbon depletion factor, with increasing n up to $n = 300\ \mathrm{cm}^{-3}$. Γ_{rec} and Γ_{pe} are comparable throughout, with Γ_{rec} tending to somewhat exceed Γ_{pe}. Cloud temperatures similar to these observed (e.g., by Spitzer, Cochran, and Hirshfeld 1974) can only be obtained for $\delta = 0.2$. For the case of $\tau_{\mathrm{uv}} \approx 2.5\ \tau_v$, Γ_{pe} predominates over Γ_{rec} by a factor of ~3 in diffuse clouds, and cloud temperatures similar to those observed can be obtained for $\delta \approx 0.5$ and $n \leqslant 100\ \mathrm{cm}^{-3}$.

The time t_{eq} for a cloud to achieve an equilibrium H_2 concentration of $f/2$ is given by HWS to be $t_{\mathrm{eq}} = f/2Rn$, or $\sim 4 \times 10^8 f/n$ years for $R = 3.7 \times 10^{-17}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$. With a mean cloud lifetime of a few times 10^6 years, most of the clouds in Table 1 should be in equilibrium. If a cloud is not yet in equilibrium, or if there exist time-dependent density fluctuations, caused, for instance, by shocks, then $(1 - f)$ may be higher than in the model calculations in Table 1. This will cause an increase in Γ_{rec}. However, for $n < 100\ \mathrm{cm}^{-3}$ we find that H atom excitation of C II dominates the cooling function, so that the cooling rate will also be proportional to $(1 - f)$. Therefore for the case of $\tau_{\mathrm{uv}} = \tau_v$, the temperatures should not be very different from these listed in Table 1A. For the case of $\tau_{\mathrm{uv}} = 2.5\ \tau_v$, an increase in $(1 - f)$ would tend to decrease the cloud temperature compared with equilibrium value since Γ_{pe}, the dominant mechanism in this case, does not depend on $(1 - f)$ whereas the cooling rate due to H atoms does.

In conclusion, if the albedo of interstellar dust in the 912–1200 Å region is high (~0.9), available heating mechanisms cannot explain observed cloud temperatures without a perhaps excessive degree of depletion of carbon. If the albedo in this wavelength region is ~0.5, however, then with a modest degree of depletion of carbon ($\delta \approx 0.5$) attributable to a normal abundance of graphite grains, the photoelectron heating mechanism can probably explain observed cloud temperatures.

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