## THE FORMATION OF CONDENSATES ON DUST IN INTERSTELLAR CLOUDS

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#### **ABSTRACT**

Observational data on the abundance of  $H_2O$  ice, CO frost, and a carbonaceous condensate in the Taurus cloud are used to estimate sticking efficiencies  $S_X^*$  for O and C on dust in this cloud, where  $S_X^*$  is the efficiency factor leading to molecule formation and retention on dust.  $S_0^*$  is found to be very small  $[\sim 2 \times (10^{-3}-10^{-4})]$  when conditions are such that a monolayer of ice has not formed on dust. When a monolayer is present  $S_0^* \sim 6 \times (10^{-2}-10^{-3})$ , where the range of  $S_0^*$  corresponds to cloud lifetimes of 0.3–3 Myr respectively. The threshold extinction  $A_V^0$  for ice accretion is suggested to be related to the formation of this monolayer. A comparison with conditions in the  $\zeta$  Oph cloud B shows no more than a few monolayers of ice have formed on dust in this object.

 $S_{\rm C}^*$  also shows a reduction at  $A_V \sim A_V^0$ , suggesting that the presence of a monolayer of ice also influences the accretion of carbonaceous material. The overall sticking efficiency for CO molecules on the dust in Taurus is  $S_{\rm CO} \sim 3.7 \times (10^{-2}-10^{-3})$ . These low values likely reflect the role of  $H_2$  formation and cosmic rays on desorption of accreted molecules.

Subject headings: dust, extinction — ISM: clouds — molecular processes

#### 1. INTRODUCTION

The accretion of atoms and molecules on dust grains leads to the depletion of gaseous elements and to the formation of coatings which may take the form of refractory components or ices such as solid H<sub>2</sub>O and CO (Whittet 1992). Considerable observational data now exists on the infrared spectra of ices in dense clouds (Whittet et al. 1988; Tanaka et al. 1990; Whittet & Duley 1991; Smith, Sellgren, & Brooke 1993) and on the depletion of elements in diffuse clouds (Morton 1975; Jenkins, Savage, & Spitzer 1986; Cardelli, Savage, & Ebbets 1991; Savage, Cardelli, & Sofia 1992; Cardelli et al. 1993; Federman et al. 1993). The depletion of elements from the gas phase is presumed to occur when these elements are incorporated in dust, either as dust is formed (Field 1974) or dynamically in the interstellar medium (Snow 1975; Barlow & Silk 1977; Duley & Millar 1978; Gail & Sedlmayr 1986; Joseph 1988). In dust clouds the primary mechanism for depletion would appear to be via the formation of molecules directly on grains (Jones & Williams 1984) which are then retained, or by the freezing out of molecules resulting from gas phase chemistry (Willacy & Williams 1993). A recent study (Smith et al. 1993) shows that the  $A_V$  threshold,  $A_V^0$ , for the accretion of  $H_2O$  and hydrocarbon condensates on dust grains in the Taurus dark cloud as implied by enhanced extinction at 3.45  $\mu$ m is identical. This observation shows that accretion of atoms leading to mantle formation is inefficient in clouds with  $A_{\nu} < A_{\nu}^{0}$  and raises several important questions as to the mechanism involved in the depletion of elements in these lightly reddened objects. For example: (1) what are the relative atomic sticking efficiencies leading to molecule formation on dust in diffuse and dense clouds, (2) what is the origin of the extinction threshold  $A_{\nu}^{0}$ , and (3) how does  $A_{\nu}^{0}$  relate to ambient interstellar conditions and the properties of dust grains? Finally, (4) what is the role of in situ dynamic accretion processes in determining elemental depletions in diffuse interstellar clouds? Our analysis is limited to the Taurus cloud which has been chosen because it is a quiescent object with minimum perturbation due to star formation where the available data indicate a clear threshold in  $A_V$ .

In this paper, we suggest that the transition from inefficient to efficient accretion of atoms by interstellar dust grains occurs when (on average) no more than a few monomolecular layers of  $H_2O$  molecules have been created on dust. When less than one monolayer is present, atoms such as C, N, O, S and others which react to form volatile hydrides on dust grains are efficiently returned to the gas. When a monolayer has been established, efficient mantle growth is possible as the atomic sticking probability leading to molecule formation increases dramatically. A mixed  $H_2O/\text{hydrocarbon}$  condensate is the result of this accretion. The threshold  $A_V^O$  which signals this transition may reflect the timescale for creation of the monomolecular  $H_2O$  layer.

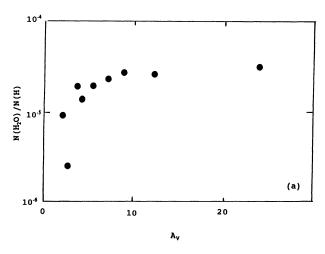
## 2. CONDENSATES IN THE TAURUS DARK CLOUD

Column densities for  $H_2O$  ice, CO frost, and a carbonaceous component (3.45  $\mu m$  absorber) have been obtained for the Taurus dark cloud using the data of Smith et al. (1993) and Whittet et al. (1989). These column densities, N, were estimated from the optical depth  $\tau$  and FWHM,  $\Delta v$  (cm<sup>-1</sup>) using the approximation

$$\tau \Delta v = NA,\tag{1}$$

where A is the integrated absorbance (cm per molecule). Values of  $\Delta v$  and A for individual condensates are given in Table 1. The column density of hydrogen has been taken to be  $N_{\rm H}=1.9\times10^{21}~A_{\rm V}~({\rm cm}^{-2})$ . On this basis, the relative abundances of condensates, plotted versus  $A_{\rm V}$  in Figure 1, are taken to represent the fractional abundance of these three dust components in the Taurus clouds. The hydrocarbon component, as inferred from the 3.45  $\mu$ m absorption wing, is likely more representative of the background underlying the narrow aliphatic absorption

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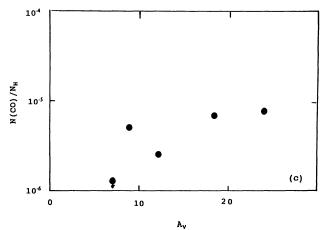


Fig. 1.—(a)  $N({\rm H_2O})/N({\rm H})$  for Taurus cloud vs.  $A_V$ ; (b)  $N({\rm CH_2})/N({\rm H})$  vs.  $A_V$ ; (c)  $N({\rm CO})/N_{\rm H}$  vs.  $A_V$ .

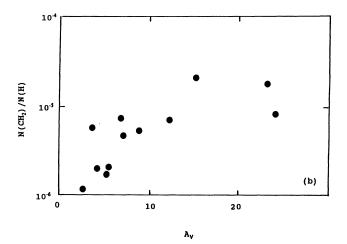
features detected by Sandford et al. (1991) and Pendleton et al. (1994) than of these features themselves.

These data show that  $N(\rm H_2O)/N_{\rm H}$  and  $N(\rm CH_2)/N_{\rm H}$  both decrease dramatically near  $A_V^0=2.6$ . In the case of  $\rm H_2O$  ice,  $N(\rm H_2O)/N_{\rm H}\approx 4\times 10^{-5}$  at high values of  $A_V$  decreasing to  $\sim 4\times 10^{-6}$  near  $A_V^0$ . For the CH<sub>2</sub> condensate,  $N(\rm CH_2)/N_{\rm H}\approx 9\times 10^{-6}$  at large  $A_V$ , decreasing to less than  $2\times 10^{-6}$  near  $A_V^0$ . The relative abundance of CO frost also drops abruptly near  $A_V=6$ .

The rapid drop in  $N(H_2O)/N_H$  near  $A_\nu^0$  is consistent with either a rapid decrease in the density of the gaseous species responsible for the formation of  $H_2O$  ice, i.e., O atoms, or with a change in sticking and reaction probability of O atoms on dust under these conditions. Since O atoms are known to be relatively abundant in the gas in diffuse clouds such as  $\zeta$  Oph,

 $\begin{tabular}{ll} TABLE & 1 \\ SUMMARY OF $\Delta v$ and $A$ Adopted for Dust Components \\ \end{tabular}$ 

Component	A (cm per molecule)	$\Delta v \ (\text{cm}^{-1})$	Reference
H <sub>2</sub> O ice	$2.0 \times 10^{-16}$	360	Allamandola & Sandford (1988)
CO frost	$1.7 \times 10^{-16}$	7	Whittet & Duley (1991)
CH <sub>2</sub>	$7.4 \times 10^{-18}$	22	Sandford et al. (1991)



where  $A_V = 1.0$  (Cardelli et al. 1991) it is unlikely that they would be less abundant in clouds where  $A_V \approx A_V^0$  than in those with  $A_V > A_V^0$ . As a consequence, the rapid decrease in  $N({\rm H_2O})/N_{\rm H}$  near  $A_V^0$  is probably due to a decrease in the sticking probability under these conditions. A similar decrease likely occurs for C atoms.

# 3. H<sub>2</sub>O MONOLAYER ON DUST

With a density of  $\rho \approx 1~{\rm g~cm^{-3}}$ , each  $\rm H_2O$  molecule in  $\rm H_2O$  ice occupies a volume  $V=3.0\times 10^{-23}~{\rm cm^3}$ . A monomolecular layer of  $\rm H_2O$  ice will then contain  $\sim V^{1/3}\rho/M=1.05\times 10^{15}$  molecules cm<sup>-2</sup>, where M is the molecular weight of an  $\rm H_2O$  molecule. The integrated surface area of interstellar dust grains is  $\epsilon=2.1\times 10^{-21}n~{\rm cm^2}$ , where n is the space density of H nuclei (Duley & Williams 1984). Then a single layer of  $\rm H_2O$  ice on dust grains yields  $n(\rm H_2O)/n=2.2\times 10^{-6}$ . The adsorption properties of dust grains would be expected to change discontinuously when this layer was complete (Williams 1993). The similarity between this value of  $n(\rm H_2O)/n=(2.2\times 10^{-6})$  and those of  $N(\rm H_2O)/n_H$  near  $A_V^0$  suggests that the threshold for the accretion of  $\rm H_2O$  ice on dust is related to the formation of this layer. The rate of formation of ice on dust is

$$R_{\rm H_2O} = n_{\rm O} S_{\rm O}^* \pi a^2 n_a v_{\rm O} \, \, {\rm cm}^{-3} \, {\rm s}^{-1} \,\,, \tag{2}$$

where  $n_{\rm O}$  and  $n_{\rm g}$  are the space densities of oxygen atoms and dust grains, respectively,  $v_{\rm O}=(2.55~kT/m)^{1/2}$  is the velocity of an O atom of mass m at temperature T, a is the grain radius and  $S_{\rm O}^*$  is the effective sticking efficiency for  $H_2O$  formation, i.e., for the formation and retention of an  $H_2O$  molecule on dust. With  $\pi a^2 n_{\rm g} \sim 2.1 \times 10^{-21} n$ ,

$$R_{\rm H_{2O}} = 7.6 \times 10^{-18} n_{\rm O} n S_{\rm O}^* (T)^{1/2} \, \rm cm^{-3} \, s^{-1}$$
 (3)

A density  $n({\rm H_2O})/n = 2.2 \times 10^{-6}$  on dust grains (i.e., one monolayer) is then formed over a timescale

$$t_{\rm H_2O}^m = \frac{2.9 \times 10^{11}}{n_{\rm O} S_{\rm O}^*(T)^{1/2}} \,\mathrm{s} \ . \tag{4}$$

For a diffuse cloud such as the  $\zeta$  Oph cloud (component B) where  $n=300~{\rm cm^{-3}}$ ,  $n_{\rm O}\approx 3\times 10^{-4}n\approx 9\times 10^{-2}~{\rm cm^{-3}}$ , and  $T=56~{\rm K}$  (Savage et al. 1992). Then  $t_{\rm H_2O}^{\rm m}(\zeta{\rm Oph})\approx 4.3\times 10^{11}/{\rm S_O^*}~{\rm s}=0.014/{\rm S_O^*}$  (Myr). In the Taurus cloud we will take  $n_{\rm O}=10^{-4}n$ ,  $n=3\times 10^4~{\rm cm^{-3}}$ , and  $T=30~{\rm K}$  as rep-

resentative values. Then  $t_{\rm H_{2O}}^{\rm m}$  (Taurus) =  $1.8 \times 10^{10}/S_{\rm O}^{*}$  s =  $5.6 \times 10^{-4}/S_{\rm O}^{*}$  (Myr). Both  $t_{\rm H_{2O}}^{\rm m}$  (Taurus) and  $t_{\rm H_{2O}}^{\rm m}$  ( $\zeta$  Oph) are small compared to the estimated ages (0.3–3 Myr and 50 Myr, respectively) of these clouds *unless*  $S_{\rm O}^{*}$  is small.

### 4. EFFICIENCY OF H<sub>2</sub>O FORMATION ON DUST

In heavily reddened objects such as Elias 16 in Taurus  $(A_V = 23.9; \text{Smith et al. 1993})$  the abundance of  $H_2O$  ice relative to hydrogen is  $\sim 5 \times 10^{-5}$  (Fig. 1). Under these conditions  $R_{H_2O} = 4.2 \times 10^{-17} nn_O S_0^* \text{ cm}^{-3} \text{ s}^{-1}$ , so that the time required to achieve this level of ice deposition is

$$t = \frac{0.038}{n_0 S_0^*} (\text{Myr}) , \qquad (5)$$

if it is assumed that the abundance of oxygen atoms is independent of time. In general  $n_0$  will be time dependent so that the timescale  $t_d$  for accretion to a level  $n(H_2O)/n = 5 \times 10^{-5}$  is obtained from

$$\int_{0}^{t_d} n_{\rm O}(t)dt = \frac{0.038}{S_{\rm O}^*} \,({\rm Myr}) \,. \tag{6}$$

This situation is complicated by desorption mechanisms such as cosmic-ray heating (Léger, Jura, & Omont 1985; Willacy & Williams 1993) or spot-heating due to the formation of  $H_2$  or other molecules (Allen & Robinson 1975; Duley 1976; Willacy, Williams & Duley 1994) which return molecules to the gas phase subsequent to accretion. We will assume that, apart from the incorporation of O atoms in CO, and silicates, the only other major source of O atom depletion in these clouds will be via accretion on dust grains to form  $H_2O$  ice.  $S_0^*$  will then be an effective sticking efficiency for O atoms leading to the formation and retention of an  $H_2O$  molecule. Then

$$n_{\mathcal{O}}(t) = n_{\mathcal{O}}(\mathcal{O})e^{-kt} \,, \tag{7}$$

where  $k = S_0^* \pi a^2 n_a v_0 = 39.7 S_0^* (Myr)^{-1}$  and

$$e^{-kt_d} = 1 - \frac{1.50}{n_0(O)},$$
 (8)

where  $t_d$  is the accretion time. Taking  $n(O) = 10^{-4} n = 3$  cm<sup>-3</sup>.

$$t_d = \frac{0.017}{S_0^*} \,(\text{Myr}) \,, \tag{9}$$

so that  $S_0^* = 5.7 \times (10^{-2} - 10^{-3})$  for a typical accretion time  $t_d = 0.3 - 3$  Myr (Herbst & Millar 1991). This range of  $S_0^*$  is then compatible with the accretion and retention of ice to the level  $n(H_2O)/n = 5 \times 10^{-5}$ .

At  $A_V \sim A_V^0$  a monolayer of  $H_2O$  ice will accrete on dust  $[n(H_2O)/n = 2.2 \times 10^{-6}]$  over a similar timescale. This yields  $S_0^*(m) = 1.9 \times (10^{-3}-10^{-4})$  as the effective efficiency for  $H_2O$  formation and retention in the absence of a monolayer on dust. Using  $S_0^*(m) = 1.0 \times 10^{-3}$  as an average value and the conditions of the  $\zeta$  Oph cloud (component B), one obtains  $k = 5.3 \times 10^{-4}$  (Myr)<sup>-1</sup>. Then, with  $n_O(O) = 3 \times 10^{-4}n = 9 \times 10^{-2}$  cm<sup>-3</sup>,  $n(H_2O)/n \sim 8.0 \times 10^{-6}$ .

### 5. FORMATION OF CARBONACEOUS CONDENSATE

If the 3.45  $\mu$ m absorption band measured by Smith et al. (1993) in spectra of field stars behind the Taurus cloud is identified with the presence of CH<sub>2</sub> functional groups, then the strength of this feature can be used to determine the amount of

carbonaceous condensate along sight lines in Taurus. Future observations may permit a similar analysis to be carried out for diffuse cloud sight lines. At large  $A_V$ ,  $N(CH_2)/N_H \approx$  $9 \times 10^{-6}$  decreasing to  $\sim 4 \times 10^{-6}$  for  $A_V \approx A_V^0$  (Fig. 1). With  $k = 1.45 \times 10^{-12}$  S<sub>C</sub>\* s<sup>-1</sup> and taking  $n_C(O)/n = 5 \times 10^{-5}$ ,  $S_C^* t \approx 4.3 \times 10^{-3}$  (Myr) at large  $A_V$  suggesting that  $S_C^* \approx$  $1.4 \times (10^{-2}-10^{-3})$ .  $S_C^*$  is therefore somewhat smaller than  $S_O^*$ under the same conditions, perhaps reflecting the higher volatility of CH<sub>4</sub> relative to that of H<sub>2</sub>O. However, this value of S<sup>\*</sup><sub>C</sub> relates only to the creation of CH<sub>2</sub> functional groups on dust. Other carbon-bearing functional groups are also expected to be present along with CH<sub>2</sub> (Duley & Williams 1983; Sandford et al. 1991). As a result, the relative abundance of carbon in the carbonaceous condensate will likely be 2-3 times larger than that adopted for CH<sub>2</sub>. This would increase  $S_C^*$  to  $\simeq 3 \times 10^{-2}$  $10^{-3}$ ). Estimated values for  $S_{\rm C}^{*}$  under the conditions of the  $\zeta$  Oph cloud (component B) are  $6.4 \times 10^{-4}$  if  $N({\rm CH_2})/N_{\rm H} \simeq$  $10^{-6}$  in this object for a total S\* of (1.3-1.9)  $\times$   $10^{-3}$ 

#### 6. STICKING EFFICIENCY FOR CO

Estimates of the relative abundance of gaseous and condensed CO in the Taurus cloud (Whittet et al. 1989) show that CO is significantly depleted from the gas phase when  $A_V > 5$ . With  $k = 9.5 \times 10^{-13} \, S_{\rm CO} \, {\rm s}^{-1}$ 

$$n_{\text{CO}}^{S}(t) = n_{\text{CO}}(O)[1 - e^{-kt}],$$
 (10)

where  $n_{CO}^{S}(t)$  is the space density of CO frost after time t. The density of gaseous CO is

$$n_{\rm CO}(t) = n_{\rm CO}(O)e^{-kt}$$
 (11)

Then

$$\frac{n_{\text{CO}}^{S}(t)}{n_{\text{CO}}(t)} = \frac{[1 - e^{-kt}]}{e^{-kt}} \,. \tag{12}$$

This ratio is  $\sim 0.4$  in heavily reddened regions of the Taurus cloud (Whittet et al. 1989) so that

$$S_{\rm CO} = \frac{0.011}{t(\rm Myr)} \,. \tag{13}$$

Then with t = 0.3-3 Myr,  $S_{CO} = 3.7 \times (10^{-2}-10^{-3})$ . On this basis,  $n_{CO}(O) = 3.0 \times (10^{-4}-10^{-5})n$  cm<sup>-3</sup>.

This result assumes that CO sticks with equal efficiency to both small and large dust grains. This may be incorrect since small grains are subject to temperature fluctuations and in any case are on average warmer than large grains. With the assumption that only large grains are effective in accreting CO,  $\pi a^2 n_g \sim 2.5 \times 10^{-22} n$  (Duley & Williams 1984) and  $k = 1.1 \times 10^{-13} S_{\rm CO} {\rm s}^{-1}$ . Then  $S_{\rm CO} = 0.097/t$  (Myr) = 0.3–0.03 for 0.3 < t < 3 Myr.

## 7. DISCUSSION

Column densities of  $H_2O$  ice, carbonaceous condensate, and CO frost in Taurus can reach observed levels only if a relatively efficient condensation process is occurring under these temperature and density conditions on the timescale that is available. In general, this requires that  $S_X$  takes the values given in Table 2. For O and C these values are  $10-10^2$  times smaller than those calculated for sticking on solid  $H_2O$  (Williams 1993). However, it must be remembered that  $S_0^*$  and  $S_0^*$  are derived only for the combined process (sticking-

TABLE 2

CALCULATED VALUES OF STICKING EFFICIENCIES FOR TYPICAL DENSE AND DIFFUSE CLOUD CONDITIONS

Sticking Efficiency	$n = 3 \times 10^4 \text{ cr}$ $t = 3 \times 10^6 \text{ yr},$		$n = 3 \times 10^{2} \text{ cm}^{-3}, T = 56 \text{ K},$ $t = 50 \times 10^{6} \text{ yr}$
S <sub>0</sub> *	$6 \times 10^{-3}$	$6 \times 10^{-2}$	$2 \times (10^{-3} - 10^{-4})$ $1.6 \times 10^{-3}$
S <sub>c</sub> *	$3.5 \times 10^{-3}$	$3.5 \times 10^{-2}$	
S <sub>co</sub>	$3.7 \times 10^{-3}$	$3.7 \times 10^{-2}$	

reaction-retention of products) which will lead to smaller values of  $S_X$  than those derived for sticking alone, if the adsorbed atom can react to form a volatile species such as  $H_2O$  or  $CH_4$ . Indications are that  $S_X^*$  may be even smaller ( $\sim 10^{-4}$ ) for incidence on grain surfaces in diffuse clouds, although firm data will only be possible when a quantitative limit is obtained from observational data on column densities for  $H_2O$  ice, CO frost, and the 3.45  $\mu$ m carbonaceous absorber

in objects such as  $\zeta$  Oph. The predicted optical depth for the 3.05  $\mu$ m H<sub>2</sub>O ice absorption band in  $\zeta$  Oph is 5.9  $\times$  10<sup>-3</sup>.

 $S_X^*$  for other atoms such as N, P, S, and Cl that also have volatile hydrides are expected to be similar to those for O and C under diffuse and dense cloud conditions. As a result, the depletion of these elements in diffuse clouds will be small compared to elements such as those of the iron group which do not form volatile hydrides. For example, with  $S_S^* = 6 \times 10^{-3}$  for sulphur, the logarithmic depletion of S after 50 Myr in the  $\zeta$  Oph cloud would be  $D_S = -0.05$ . The incremental depletion over the same timescale for an element such as Fe (assuming  $S_{Fe}^* \approx 0.5$ ) would be  $D_{Fe} = -3.12$ . This suggests that dynamic accretion may play an important role in determining the depletion pattern of elements with nonvolatile hydrides in diffuse clouds but will have little effect on the depletion of elements with volatile hydrides.

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