CHEMICAL EFFECTS OF INTERSTELLAR GRAINS

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ABSTRACT The chemical effects of interstellar grains are briefly reviewed. Their dominant chemical role is to catalyze the formation of H_2 which is the seminal molecule for efficient gas phase chemistry. In regions of at least moderate extinction grains accumulate molecular mantles of CO, H_2O, etc. Solid state chemistry in such mantles may produce molecules of a type or in an abundance not achievable in the interstellar gas. Return of mantle material to the gas can - at least transiently - dominate gas phase chemistry. It is argued that the freeze-out of heavy atomic and molecular species on to grain surfaces limits the time available for chemistry, restricts molecular cloud chemistry to a "young" character, and suggests that chemical models of molecular clouds must have cyclic dynamics. Such models are briefly described.

2. Introduction

Some of the chemical effects of interstellar grains are listed in Table 1. Obviously, atoms locked in grains are unavailable in the interstellar gas and, thus, the presence of grains immediatly affects possible chemistry. Table 2 indicates the approximate fraction of some elements available in the gas. The sensitivity of the chemistry of molecular clouds to, e.g., the C:O ratio has been explored by Watt (1984).

Table 1. **Chemical Effects of Interstellar Grains**

Lock up certain elements (Si, Fe, Mg) in refractory cores
Catalyze H_2 formation; formation of other molecules?
Extinguish starlight, shield cloud interiors
Heat diffuse gas by photoelectric effect
Provide sites of mantle formation
Mantle processing in solid state
Storage of molecular mantles, release to gas
Role of grains and mantles in star formation

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Table 2. Abundances of elements in gas and dust (by number)

Element	Fraction in	
	gas	dust
C	0.5	0.5
N	0.6	0.4
O	0.6	0.4
Mg	0.2	0.8
Si	0.05	0.95
S	0.6	0.4
Fe	0.02	0.98
Others	0	1.0

Perhaps the most significant effect of grains on interstellar chemistry is the efficient catalysis of H_2 in surface reactions. The observations require that in diffuse clouds almost every H atom striking a grain surface must leave as part of an H_2 molecule. Modern views of the nature of grains in terms of silicaceous and carbonaceous materials allow a more detailed description of the surface reaction, and the state of the nascent H_2 molecule can be predicted (Duley and Williams 1986). It appears likely that H_2 is kinetically and vibrationally excited on ejection from grain surfaces. However, radiative and collisional relaxation will generally ensure that the molecule ends up in an excited rotational state from which radiative relaxation is relatively slow.

The formation of molecules other than H_2 may also occur on grains. The observation of H_2O ice mantles in moderate extinction interstellar clouds implies that $O \rightarrow H_2O$ conversions occur *in situ* (Jones and Williams 1984). Ion reactions at charged defect sites on grains are sufficiently exothermic that products are ejected (e.g. Jones and Williams 1986 and references therein). The significance of surface chemistry to diffuse cloud chemistry is at present uncertain (Mann and Williams 1984, 1985). However, there is no doubt that the molecular mantles play an important part in the chemistry of dark clouds.

3. Mantle Growth and Gas Phase Chemistry

Mantle composition reflects the current chemical composition of the gas, responds to chemical processing in the solid state, and is affected by any possible mantle limitation processes. Much laboratory and theoretical work has been performed describing the nature of mantle material, and comprehensive models of cloud chemistry, including both gas and solid components have been constructed (cf. d'Hendecourt et al. 1982). Models of specific molecular clouds such as TMC1, on simple assumptions of freeze-out and hydrogenation reactions, are in reasonable agreement with observations and expectations (Brown and Charnley 1988). In such models an "age" of the cloud can be inferred: for TMC1 it appears to be about 2×10^6 yr.

Such simple static models, however, suffer from a number of defects. For example: can freeze-out of heavy species on to grains occur without limit? Another class of objects seems better described by clouds which are undergoing collapse, in which gas phase chemistry and freeze-out of heavy species on to grains are simultaneously occurring (cf. Tarafdar, this volume). The Hot Core in Orion has a number of interesting features which make it distinct from cold molecular clouds: e.g., NH_3, CH_3OH and HDO seem strongly enhanced, and the HCN/HNC ratio is anomalously high. An explanation of this behaviour has been given by Pauls et al. (1983) in terms of the evaporation of molecular mantles (formed during a collapse phase) following star formation. This suggestion has been explored in detail by Brown et al. (1988) who conclude that such a model is capable of accounting for molecular abundances observed in the Hot Core. Some molecules (e.g. HCN, H_2CO) in the Hot Core were apparently formed in the cold gas, stored in the mantle and released in the hot phase, while others (H_2O, NH_3) arise from hydrogenation of atoms in the mantles. In particular, it appears that NH_3 must be deuterated (to NH_2D) on grain surfaces during the cold phase.

4. Dynamics

While it is encouraging that models like that of Brown et al. (1988) incorporating both gas and solid phase chemistry, cloud collapse and star formation have met with some success, it is clear that the actual situation in star formation regions will be considerably more complicated. The association of dark clouds and young stars has been well studied (cf. Fuller and Myers 1987) and the prevalence of high velocity flows from such stars is well established (Lada 1985). Charnley et al. (1988a) have explored the chemistry in a model of molecular clouds in which a sequence of events is supposed to occur: first, the wind of a newly formed star erodes dense cloud material; this mass-loaded wind is brought to local rest by a shock, accumulates and forms a new dense clump in which chemistry and mantle formation occur and from which a new generation star is formed. In such models chemistry is never in steady state, and chemical abundances reflect to some extent the star forming activity. The chemistry is generally "young" in the sense that not all the available carbon is processed into CO.

Such models imply that chemical and dynamical states in molecular clouds are closely linked and cyclic. Charnley et al. (1988b) have addressed the question: does the chemical state of the gas follow the dynamical cycle or does chemical chaos ensue? In two illustrative models, involving both long and short cycle times, their results indicate that chemical limit cycles exist and, therefore, that chemistry is a proper tracer of the physical conditions in molecular clouds. At one point in each cycle mantled grains are exposed to fast stellar winds: thus, the limitation of mantle growth has a natural explanation, yet mantle growth has its restricting effect on the chemistry. In the repeated cycling of the material, all memory of the initial conditions is lost. Such models predict the abundances of molecules point-by-point in clouds. Thus, the predictions of the model may be tested in relatively nearby clouds. Of these B5 (Goldsmith et al. 1986) appears to be an ideal example. It contains IRAS sources, dense clumps of gas, and molecular flows. Point-by-point molecular studies of B5 should indicate the validity of the dynamical/chemical model for molecular clouds.

5. Conclusion

Dust grains have a profound effect on interstellar chemistry in diffuse clouds by shielding cloud interiors, by photoelectric heating, and - primarily - by catalyzing the formation of H_2 (without which the chemistry is strongly suppressed). In dark clouds, mantles accummulate on grains and solid state reactions occur. This further loss of material from the gas influences chemical developments there. The return of mantle material, possibly stimulated by star formation, can lead to important observational consequences. The timescale for freeze-out is relatively short, and implies the need for efficient mantle removal. In the models described here, this mantle removal is associated with star formation.

REFERENCES

Brown, P.D., Charnley, S.B. & Millar, T.J. 1988 Mon. Not. R. astr. Soc. 231, 409.
Brown, P.D. & Charnley, S.B. 1988 in preparation.
Charnley, S.B., Dyson, J.E., Harquist, T.W. & Williams, D.A. 1988a. Mon. Not. R. astr. Soc. 231, 269.
Charnley, S.B., Dyson, J.E., Harquist, T.W, & Williams, D.A. 1988. Mon. Not. R. astr. Soc. in press.
Duley, W.W. & Williams, D.A. 1986. Mon. Not. R. astr. Soc. 223, 177.
Fuller. G.A. & Myers. P.C. 1987, Physical Processes in Interstellar Clouds, G.E. Morfill & M. Scholer (eds), D. Reidel Pub. Co., p.137
Goldsmith, P.F., Langer, W.D. & Wilson, R.W. 1986. Astrophys. J. Lett. 303, L11.
d'Hendecourt, L.B., Allamandola, L.J., Baas, F. & Greenberg, J.M. 1982. Astron. Astrophys. 109, L12.
Jones, A.P. & Williams, D.A. 1984, Mon. Not. R. astr. Soc. 209, 955.
Jones, A.P. & Williams, D.A. 1986 Mon. Not. R. astr. Soc. 219, 441.
Lada, C. 1985. Ann. Rev. Astron. Astrophys. 23, 267.
Mann, A.P.C. & Williams, D.A. 1984 Mon. Not. R. astr. Soc. 209, 33.
Mann, A.P.C & Williams, D.A. 1986 Mon. Not. R. astr. Soc. 213, 295.
Pauls, T.A., Wilson, T.L., Bieging, J.H. & Martin, R.N. 1984. Astron. Astrophys. 124, 33.
Tarafdar, S. 1988, this volume.
Watt, G.D. 1984. Mon. Not. R. astr. Soc. 212, 93.