THE ASTROPHYSICAL JOURNAL, 192:29–32, 1974 August 15

THE FRACTIONAL IONIZATION IN DENSE INTERSTELLAR CLOUDS

M. OPPENHEIMER AND A. DALGARNO
Center for Astrophysics, Harvard College Observatory and Smithsonian Astrophysical Observatory
Received 1974 January 14; revised 1974 March 7

ABSTRACT

It is pointed out that charge-transfer reactions of complex molecular ions with neutral metal atoms significantly increase the fractional ionization in a dense interstellar cloud bombarded by high-energy cosmic rays. The mean time for ambipolar diffusion becomes comparable to the cloud lifetime only when densities exceed 10^6 cm^{-3} and the magnetic field will retard the gravitational collapse of clouds of smaller particle density. A brief discussion is given of some other consequences of the relatively high fractional ionization.

Subject headings: abundances, nebular — atomic processes — interstellar matter — molecules, interstellar

I. INTRODUCTION

The degree of ionization of a dense interstellar cloud plays a fundamental role in chemical reaction schemes for molecular formation (cf. Herbst and Klemperer 1973; Dalgarno, Oppenheimer, and Berry 1973*a*; Watson 1973; Black and Dalgarno 1973) and in the determination of the thermodynamic properties of the clouds. The fractional ionization also controls the coupling of the cloud to the galactic magnetic field. Because of the coupling, the magnetic energy density increases as the cloud collapses, and the collapse is retarded and may be prevented (Spitzer 1968).

Ambipolar diffusion (Mestel and Spitzer 1956) enables the charged species to drift out of a collapsing cloud and cause the exclusion of the magnetic field. In diffuse clouds the fractional ionization is high and the ambipolar diffusion time is long (Spitzer 1968; Nakano and Tademaru 1972). In dense clouds ion-molecule reactions (cf. Herbst and Klemperer 1973) tend to produce a reduced fractional ionization, and the magnetic field may be less effective in preventing gravitational contraction.

II. ION CHEMISTRY

In large interstellar clouds with densities n exceeding 10^3 cm^{-3}, most of the hydrogen is in the form of H_2 and no ultraviolet radiation penetrates. The primary ionization process is then cosmic-ray ionization of H_2. The products are H_2^+ and H^+ in the ratio of 95:5 (cf. de Jong 1972). H_2^+ immediately reacts with H_2:

$$H_2^+ + H_2 \rightarrow H_3^+ + H\,; \tag{1}$$

and H^+ is destroyed by charge exchange with atomic oxygen

$$H^+ + O \rightarrow O^+ + H \tag{2a}$$

and with molecular oxygen

$$H^+ + O_2 \rightarrow H + O_2^+\,. \tag{2b}$$

Reaction (2b) probably remains rapid at low temperatures whereas reaction (2a) becomes slow. H_3O^+ is formed by the reactions

$$H_3^+ + O \rightarrow OH^+ + H_2\,, \tag{3}$$

$$O^+ + H_2 \rightarrow OH^+ + H\,, \tag{4}$$

followed by

$$OH^+ + H_2 \rightarrow H_2O^+ + H\,, \tag{5}$$

$$H_2O^+ + H_2 \rightarrow H_3O^+ + H\,; \tag{6}$$

and HCO^+ is formed by

$$H_3^+ + CO \rightarrow HCO^+ + H_2 \tag{7}$$

(Herbst and Klemperer 1973).

The helium atoms are also ionized by cosmic rays at about 0.1 times the H_2 ionization rate ζn. The He^+ ions then react with CO,

$$He^+ + CO \rightarrow C^+ + O + He\,, \tag{8}$$

to form carbon ions (Herbst and Klemperer 1973). These ions are destroyed by

$$C^+ + O_2 \rightarrow CO^+ + O \tag{9}$$

$$\rightarrow CO + O^+ \tag{10}$$

(Herbst and Klemperer 1973) and probably by

$$C^+ + H_2 \rightarrow CH_2^+ + h\nu \tag{11}$$

(Black and Dalgarno 1973). The abundance of O_2 in dense clouds is uncertain, but process (11) leads to a low C^+ abundance in any event. CH_2^+ reacts rapidly with H_2 to form CH_3^+:

$$CH_2^+ + H_2 \rightarrow CH_3^+ + H \tag{12}$$

(Huntress and Kim 1973) so that all the ionizations involving H_2 and He result in the formation of complex molecular ions. The ions are destroyed by the dissociative recombination processes

$$O_2^+ + e \rightarrow O + O\,, \tag{13}$$

$$HCO^+ + e \rightarrow CO + H\,, \tag{14}$$

$$\begin{aligned} H_3O^+ + e &\rightarrow 2H + OH \\ &\rightarrow H_2O + H \\ &\rightarrow H_2 + OH\,, \end{aligned} \tag{15}$$

$$\begin{aligned} H_3^+ + e &\rightarrow H_2 + H \\ &\rightarrow 3H\,, \end{aligned} \tag{16}$$

and

$$\begin{aligned} CH_3^+ + e &\rightarrow CH_2 + H \\ &\rightarrow CH + H_2 \\ &\rightarrow CH + H + H\,. \end{aligned} \tag{17}$$

O_2^+ may react with N and other species to form diatomic and polyatomic ions which will be rapidly removed by dissociative recombination. CH_3^+ may react with oxygen and other neutral species to form molecular ions such as H_2CO^+ which are also rapidly removed by dissociative recombination (Dalgarno, Oppenheimer, and Black 1973*b*). The rate coefficient for reaction (13) is measured to be 2.0×10^{-7} cm^3 s^{-1} at 300° K (Mehr and Biondi 1969); that for reaction (14) is measured to be 3×10^{-7} cm^3 s^{-1} at 200° K (Leu, Biondi, and Johnsen 1973*a*); that for reaction (15) to be 1.3×10^{-6} cm^3 s^{-1} at 300° K (Leu, Biondi, and Johnsen 1973*b*); and that for reaction (16) to be 3×10^{-7} cm^3 s^{-1} at 205° K (Leu, Bondi, and Johnsen 1973*c*). The rate coefficient for reaction (17) is probably also about 10^{-6} cm^3 s^{-1}. We assume that the coefficients of (13)–(17) vary slowly with temperature; their behavior at very low temperatures is uncertain.

If reactions (13)–(17) control the removal of electrons, the total electron density is no greater than

$$n(e) \sim 10^3(\zeta n)^{1/2}\,,$$

(cf. Dalgarno *et al.* 1973*a*). For a cloud of total particle density $n \sim 10^6$ cm^{-3} and a cosmic-ray ionization rate $\zeta \sim 10^{-17}$ s^{-1}, the fractional ionization $n(e)/n$ is only 3×10^{-9}. However, the major molecular ions, such as O_2^+, HCO^+, H_3O^+, and CH_3^+, charge transfer rapidly with heavy metal atoms which are minor constituents of the interstellar medium with fractional abundances no greater than 10^{-5} to 10^{-4}. These species include Mg, Ca, Na, and Fe. Their respective singly charged ions are generally chemically inert, and the metal ions do not form the complex molecular ions that recombine rapidly. The rates of atomic ion destruction are determined by the slow process of radiative recombination with electrons, and it is these slowly recombining species which determine the ion and electron densities in dense clouds. Similar processes occur in planetary atmospheres (cf. Ferguson and Fehsenfeld 1968). The chemical reaction scheme is summarized in figure 1.

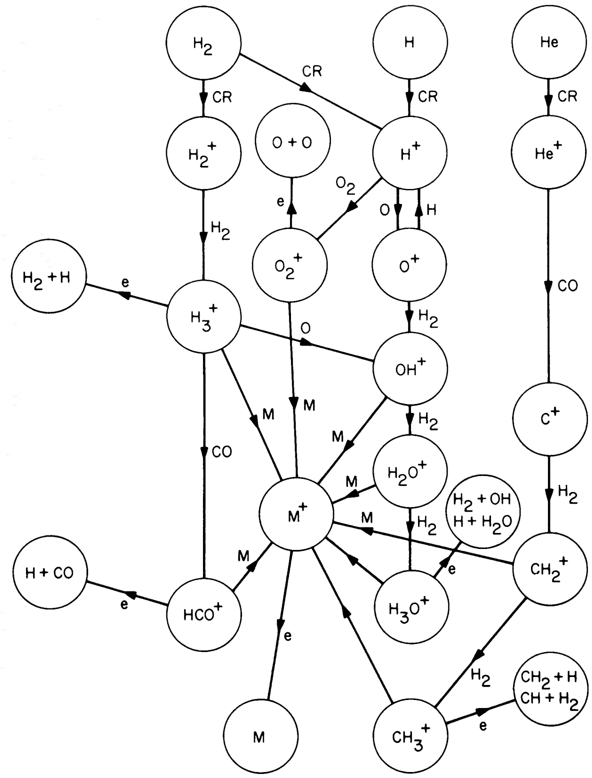

FIG. 1.—Chemical reactions which control the electron density in dense interstellar clouds.

The thermochemical data for Ca^+, Mg^+, Na^+, and Fe^+ indicate that they do not react in binary encounters with O_2, CO, H_2, or N_2 at the temperatures characteristic of the dense regions of the interstellar medium (Ferguson and Fehsenfeld 1968). On the other hand, silicon, which may charge transfer rather rapidly with HCO^+ due to a near resonance, forms singly charged ions which react with O_2. The SiO^+ ions formed may then charge exchange with heavy metal atoms. The Si^+ ions may also initiate a sequence after forming SiH_2^+ by radiative association:

$$Si^+ + H_2 \rightarrow SiH_2^+ + h\nu\,. \tag{18}$$

Let $n(M_i)$ be the density of the heavy metal atom M_i, $n(M_i^+)$ the density of the heavy metal ion M_i^+ and $n(m_j^+)$ the density of the molecular ion m_j^+. Let α_{ri} be the radiative recombination rate coefficient for M_i^+, α_j the dissociative recombination rate coefficient for m_j^+, and β_{ji} the charge-transfer rate coefficient for $m_j^+ + M_i \rightarrow m_j + M_i^+$. The electron density is

$$n(e) = \sum_i n(M_i^+) + \sum_j n(m_j^+)\,. \tag{19}$$

For an ionizing flux ζ, the electron density varies with time according to

$$dn(e)/dt = \zeta n - \sum_j \alpha_j n(m_j{}^+)n(e) - \sum_i \alpha_{ri} n(M_i{}^+)n(e) . \quad (20)$$

In steady-state equilibrium,

$$n(e) = \frac{\zeta n}{\sum_j \alpha_j n(m_j{}^+) + \sum_i \alpha_{ri} n(M_i{}^+)} . \quad (21)$$

The rate equation for the molecular ion density is

$$\frac{dn(m_j{}^+)}{dt} = \gamma_j \xi n - \alpha_j n(m_j{}^+)n(e) - \sum_i \beta_{ji} n(M_i)n(m_j{}^+) , \quad (22)$$

where γ_j is the fraction of ionizations leading to the formation of $m_j{}^+$. In equilibrium

$$n(m_j{}^+) = \frac{\gamma_j \zeta n}{\alpha_j n(e) + \sum_i \beta_{ji} n(M_i)} . \quad (23)$$

A useful simple approximation can be obtained by assuming that the rate coefficients $\alpha_j = \alpha$ and $\beta_{ji} = \beta$ are independent of j and i. Then the total density of molecular ions, $n(m^+) = \sum_j n(m_j{}^+)$, is given by

$$\sum_j n(m_j{}^+) = \frac{\zeta n}{\alpha n(e) + \beta n(M)} , \quad (24)$$

where $n(M) = \sum_i n(M_i)$ is the total density of heavy neutral atoms that undergo charge transfer with molecular ions. It follows from equation (21) that

$$n(e) = \zeta n / [\alpha n(M^+) + \alpha_r n(M^+)] . \quad (25)$$

Using equations (19), (23), and (25), we obtain

$$n(e)^3 + \frac{\beta n(m)}{\alpha} n(e)^2 - \frac{\zeta n n(e)}{\alpha} - \frac{\zeta n \beta n(M)}{\alpha \alpha_r} = 0 . \quad (26)$$

Depending upon the magnitude of the ionizing flux and the heavy atom densities $n(M)$, the electron density may vary as ζn, $(\zeta n)^{1/2}$, or $(\zeta n)^{1/3}$. The dissociative recombination coefficient α is ordinarily much greater than the radiative recombination coefficient α_r. Then in interstellar clouds ionized by high-energy cosmic rays, $n(e) > \beta n(M)/\alpha$ and it is a satisfactory approximation to adopt the formula

$$n(e) \sim \left[\frac{\zeta n \beta n(M)}{\alpha \alpha_r}\right]^{1/3} , \quad (27)$$

provided that $n(M) \gg n(e)$. The cube-root dependence occurs because nearly all the ions that exist in equilibrium are the slowly recombining atomic ions M^+, most of the molecular ions having been removed rapidly by dissociative recombination. The source of the M^+ ions is that fraction, $\beta n(M)/\alpha n(e)$, of the molecular ions that undergo charge transfer. Thus the production rate of M^+ ions is $\zeta n \beta n(M)/\alpha n(e)$. The recombination rate of M^+ ions is $\alpha_r n_e{}^2$, and formula (27) is recovered.

Because of the dependence of $n(e)$ on the one-third power of $\zeta n n(M)$, the electron density is insensitive to the magnitude of the ionizing flux and to the depletion of heavy elements.

For the rate coefficient β we adopt the value 10^{-9} cm^3 s^{-1}, somewhat smaller than the rate coefficient for the charge-transfer reaction of H_3O^+ with Ca that is extrapolated from the laboratory data at high energies (cf. Ferguson 1972). For α we take as typical 10^{-6} cm^3 s^{-1}; and for α_r, 10^{-11} cm^3 s^{-1}. Then defining a depletion factor δ by the expression

$$n(M) = 4 \times 10^{-5} \delta n ,$$

we obtain for the fractional ionization

$$\kappa = \frac{n(e)}{n} \sim \left(\frac{4 \times 10^3 \zeta \delta}{n}\right)^{1/3} . \quad (28)$$

If the ionization source is high-energy cosmic rays, ζ is of the order of 10^{-17} s^{-1} (Spitzer 1968). Observations of diffuse regions of the interstellar medium suggest an average depletion factor for heavy metals between 4 and 10 (Morton *et al.* 1973) with Ca more severely depleted (cf. Field 1974). The relative abundance of CO in dense clouds suggests that the depletion of elements is no more severe in dense than in diffuse clouds. A depletion factor near 0.1 leads to a fractional ionization κ of about $2 \times 10^{-5} n^{-1/3}$ in dense interstellar clouds.

Because the various molecular ions H_3^+, HCO^+, H_3O^+, CH_3^+, and H_3CO^+, and heavy atoms Na, Fe, Mg, and Ca, react differently, the actual situation is more complicated than that represented by equation (27) or (28). The ion H_3O^+ cannot charge transfer in collisions with Mg and Fe whereas HCO^+ can; and both H_3O^+ and HCO^+ can charge transfer with Ca and Na, which, however, may be differentially depleted. An accurate prediction of the distribution of the ionization among the various ionic species is not possible because the distribution is sensitive to depletion and because many of the rate coefficients are unknown, not only for reactions of the molecular ions with neutral atoms but also for charge-transfer reactions such as

$$Mg^+ + Na \rightarrow Mg + Na^+ , \quad (29)$$

$$Ca^+ + Na \rightarrow Ca + Na^+ , \quad (30)$$

and

$$Fe^+ + Na \rightarrow Fe + Na^+ , \quad (31)$$

which will modify the ionization distribution in dense clouds. Nevertheless, it is unlikely that the total ionization will be greatly modified by these various refinements in the chemistry. Indeed, a minimum value of κ can be obtained by assuming that sodium, which can undergo charge transfer with all the molecular ions, is the sole source of ionization. Using sodium alone, with $\delta = 0.1$ and $n(\text{Na}) = 2 \times 10^{-7}n - n(e)$, κ is reduced by a factor of 5 for $n = 10^4\ \text{cm}^{-3}$, and by a smaller factor for higher densities.

The relatively high fractional ionization that arises in the chemical scheme of figure 1 has a number of consequences. The time scale for the diffusion of electrons and ions, t_D, is about $10^{14}\kappa$ years (Spitzer 1968; Nakano and Tademaru 1972). With κ predicted to be $10^{-5}n^{-1/3}$ and a mean time of typically 10^7 years between intercloud collisions, particle densities must exceed $10^6\ \text{cm}^{-3}$ before diffusion can bring about the exclusion of the magnetic field.

The predicted values of n markedly reduce the expected abundance of HCO^+. For a cloud of density $n = 10^4\ \text{cm}^{-3}$, Herbst and Klemperer (1973) predict a value of $4 \times 10^{-4}\ \text{cm}^{-3}$ for both $n(e)$ and $n(HCO^+)$, the principal destruction mechanism for HCO^+ being dissociative recombination. Using $n(M) = 4 \times 10^{-5}\delta n$ and $\delta = 0.1$, we predict $n(e) \sim 8 \times 10^{-3}\ \text{cm}^{-3}$ and therefore $n(HCO^+) \sim 2 \times 10^{-5}\ \text{cm}^{-3}$. If the interstellar grains are negatively charged, heavy metal ions may be neutralized by a collision with a single grain. Replacing the neutralization rate $\alpha_r n(e)$ by the grain collision rate $10^{-17}n$ (which may be slightly enhanced for ions, cf. Watson and Salpeter 1972) in equation (24), we find that $n(e)$ is given by $[10^{17}\beta\zeta n(M)/\alpha]^{1/2}$. If grains are perfectly efficient for neutralizing metal ions, the fractional ionization is slightly lower than if radiative recombination dominates. Including both radiative recombination and grain neutralization, we find $n(e) = 4 \times 10^{-3}\ \text{cm}^{-3}$ for $n = 10^4\ \text{cm}^{-3}$.

The higher fractional ionization corresponding to the chemistry of figure 1 is accompanied by increased abundances of negative ions, which can produce molecules by reactions of associative detachment (Dalgarno and McCray 1972). It strengthens the suggestion of Oppenheimer and Dalgarno (1974) that OCS is formed mainly by

$$CO + S^- \rightarrow OCS + e\,, \tag{32}$$

and enhances the possibility that other molecules may form by dissociative attachment reactions following attachment of electrons to atoms and molecules in the cloud.

A study of the densities of molecular ions and a search for recombination lines of heavy metal ions in dense regions may provide observational evidence for a high fractional ionization.

That the reduction in fractional ionization due to ion-molecule reactions might alleviate the difficulty of gravitational collapse in a magnetic field was raised by Dr. M. Jura in a private communication. This work has been partly supported by the National Science Foundation.

REFERENCES

Black, J., and Dalgarno, A. 1973, *Ap. Letters*, **15**, 79.
Dalgarno, A., and McCray, R. 1972, *Ann. Rev. Astr. and Ap.*, **10**, 375.
Dalgarno, A., Oppenheimer, M., and Berry, R. S. 1973*a*, *Ap. J. (Letters)*, **183**, L21.
Dalgarno, A., Oppenheimer, M., and Black, J. 1973*b*, *Nature*, **245**, 100.
de Jong, T. 1972, *Astr. and Ap.*, **20**, 263.
Ferguson, E. E. 1972, *Rad. Sci.*, **7**, 397.
Ferguson, E. E., and Fehsenfeld, F. 1968, *J. Geophys. Res.*, **73**, 6215.
Field, G. B. 1974, *Ap. J.*, **187**, 453.
Herbst, E., and Klemperer, W. 1973, *Ap. J.*, **185**, 505.
Huntress, W., and Kim, J. K. 1973, private communication.
Leu, M. T., Biondi, M. A., and Johnsen, R. 1973*a*, *Phys. Rev.*, **A8**, 420.
———. 1973*b*, *ibid.*, **A7**, 292.
———. 1973*c*, *ibid.*, **A8**, 413.
Mehr, F. J., and Biondi, M. A. 1969, *Phys. Rev.*, **181**, 264.
Mestel, L., and Spitzer, L. 1956, *M.N.R.A.S.*, **116**, 503.
Morton, D. C., Drake, J. F., Jenkins, E. B., Rogerson, J. B., Spitzer, L., and York, D. G. 1973, *Ap. J. (Letters)*, **181**, L103.
Nakano, T., and Tademaru, E. 1972, *Ap. J.*, **173**, 87.
Oppenheimer, M., and Dalgarno, A. 1974, *Ap. J.*, in press.
Spitzer, L. 1968, *Diffuse Matter in Space* (New York: Interscience).
Watson, W. 1973, *Ap. J. (Letters)*, **183**, L17.
Watson, W. D., and Salpeter, E. E. 1972, *Ap. J.*, **174**, 321.

A. DALGARNO
Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138

M. OPPENHEIMER
Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138