

CHEMISTRY IN THE EARLY UNIVERSE

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ABSTRACT. The chemical processes which led to the formation of molecules in the early universe are described. Molecular hydrogen is formed by two sequences. In one, radiative attachment to form H^- is followed by associative detachment and in the other radiative association to form H_2^+ is followed by a chemical reaction with H. Trace amounts of HD and the molecular ion LiH^+ are formed by the reaction of D^+ with H_2 and by the radiative association of Li^+ and H. The H_2 molecular fraction in the expanding universe is about 10^{-6} .

Because they are cooling agents, hydrogen molecules are significant in the collapse of pre-galactic clouds. With increasing density the hydrogen gas is converted to molecular hydrogen by three-body recombination and emission from the rotational and vibrational levels cools the cloud and slows the rise in temperature of the gravitationally collapsing object. Ultimately though, the radiation is trapped and the temperature rises. The H_2 molecules are then destroyed by collision-induced dissociation. At still higher temperatures collisional ionization occurs, initiated most probably by the process of associative ionization.

Molecules may be significant also in galaxy formation if the explosive amplification model is correct. Heavy elements may be present in the shell of gas swept up by the blast waves of the exploded seed galaxies and chemical processes leading to the formation of molecular hydrides may take place, in a scenario analogous to the aftermath of an interstellar dissociative shock.

1. Introduction

The chemistry of the early Universe is the chemistry of the elements H and its isotope D, helium in its isotopic forms 4He and 3He and lithium in its isotopic forms 7Li and 6Li . The D, He and Li nuclei were created during the nuclear burning era with fractional abundances by number relative to protons of respectively about 5×10^{-5} , 10^{-1} and 10^{-10} . Chemistry began in the recombination epoch when the adiabatic expansion caused the temperature of the radiation to fall below about 4000K so that photoionization processes such as



were no longer able to reverse processes of radiative recombination such as



The Universe was transformed from a fully-ionized state to a nearly neutral state. The few electrons and protons, remaining after recombination, acted as catalysts in the formation of the first molecules.

In the neutral Universe, thermal contact between matter and radiation, which had been maintained by Thompson scattering of electrons and protons, was lost and matter and radiation evolved independently. Because of the red shift of the radiation, its temperature fell below that of the matter. The matter density was low and the rotational and vibrational populations of the molecular species formed in the recombination epoch were controlled by the radiation field and characterized by the temperature of the radiation field. The efficiencies of the molecular formation processes were controlled by collisions and characterized by the matter temperature.

2. Formation and Destruction Processes

Chemistry was initiated by the radiative association process



The rate coefficient has been calculated by Bates (1952), Buckingham, Reid and Spence (1952), and Ramaker and Peek (1966). It has a value of about $3.4 \times 10^{-22} T^{1.5} \text{ cm}^3 \text{ s}^{-1}$. Because the process requires the approach of H and H^+ along the repulsive $2p\sigma_u$ potential energy curve of H_2^+ , its efficiency diminishes rapidly with the kinetic temperature. The H_2^+ ions, with a level population specified by the radiation temperature, are destroyed by photodissociation



The cross sections for photodissociation of the individual vibrational levels of H_2^+ have been calculated by Dunn (1968) and the cross section for thermal distributions of vibrational levels by Argyros (1974). The threshold for photodissociation of the lowest vibrational level of H_2^+ with vibrational quantum number $v=0$ is 2.65eV and photodissociation cross section diminishes rapidly in efficiency as the radiation cools below 4000K.

Dissociative recombination,



also destroys the molecular ions. The rate coefficients for dissocia-

tive recombination of individual vibrational levels of H_2^+ have been calculated by Zhdanov and Chibisov (1978), Rai Dastidar and Rai Dastidar (1979), Derkits, Bardsley and Wadehra (1979), Zhdanov (1980) and Giusti-Suzor, Bardsley and Derkits (1983). For $v = 0$, the rate coefficient is $1.7 \times 10^{-8} (100/T)^{1/2} \text{ cm}^3 \text{ s}^{-1}$ and for $v=1$ and 2 , $1 \times 10^{-7} (100/T)^{1/2} \text{ cm}^3 \text{ s}^{-1}$.

The presence of helium in the early Universe gives rise to a rich assembly of molecular processes (Hirasawa 1969). For vibrational levels $v \geq 3$, H_2^+ ions react rapidly with He to form HeH^+ ,



Ions of HeH^+ are also produced by radiative association of protons and helium atoms,



but the process is very slow. The HeH^+ ions are mostly removed by reacting with H in the reverse of (6),



to reform H_2^+ . Rate coefficients for reactions producing and destroying HeH^+ have been listed by Roberge and Dalgarno (1982).

Once photodissociation ceases to be rapid, the H_2^+ ions react preferentially with neutral atomic hydrogen to form molecular hydrogen by charge transfer or ion-atom interchange



Process (9) was introduced into the early chemistry by Saslaw and Zipoy (1967). Its rate coefficient has been measured by Karpas, Aninich and Huntress (1979) at a kinetic temperature of about 300K for an unknown vibrational population of H_2^+ .

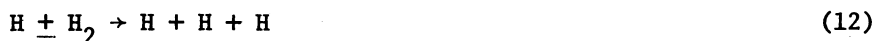
Processes that destroy H_2 include the reverse of (9), electron-impact excitation leading to dissociation,



dissociative attachment



collision-induced dissociation



and photodissociation



Cross sections for (11) have been obtained by Wadehra (1984). For thermal electrons, the cross sections are large only for high vibrational levels. Collision-induced dissociation is inhibited at low densities by radiative stabilization (Dalgarno and Roberge, 1979, Roberge and Dalgarno, 1982, Lepp and Shull 1983), and only direct excitations from the initial vibrational level into the continuum contribute to dissociation. In the radiation conditions prevailing at the time of formation of H_2 , the vibrational population of H_2 is restricted to low-lying levels and collision-induced dissociation is unimportant. Cross sections for direct photodissociation from individual vibrational levels have been presented by Allison and Dalgarno (1969a, 1969b), Glass-Maujean, Guyon and Breton (1986) and Glass-Maujean (1986). The molecular data required to calculate the probability of photodissociation following discrete absorption into the $B^1\Sigma_u^+$ and $C^1\Pi_u$ states have been given by Allison and Dalgarno (1970) and Stephens and Dalgarno (1970). Because the radiation temperature has diminished, photodissociation of H_2 is unimportant and the H_2 molecules formed after the recombination epoch survive. The rate of H_2 formation varies as the square of the density and the abundance of H_2 was limited by the amount that was formed before the density decreased in the expanding Universe.

There is a second sequence through which H_2 is formed which occurs at a later time when the negative ions of H^- formed by radiative attachment



are not destroyed by the reverse process of photodetachment



which has a threshold at 0.75eV. The H^- ions undergo associative detachment,



That reaction (15) is a source of H_2 in the interstellar gas was pointed out by McDowell (1961). Cross sections for (15) have been calculated by Broad and Reinhardt (1976), Stewart (1978) and Wishart (1979) and measured by Bryant et al. (1981), and the rate coefficients for (14) have been calculated by Dalgarno and Kingston (1963), Doughty and Fraser (1964), and de Jong (1972). Rate coefficients for (16) have been calculated by Browne and Dalgarno (1969), Bieniek and Dalgarno (1979) and Bieniek (1980), and measured by Schmeltekopf, Fehsenfeld and Ferguson (1967).

The efficiency with which reactions (14) and (16) form H_2 is diminished slightly by the destruction of H^- by mutual neutralization

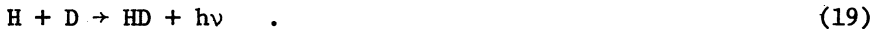


and



The rate coefficient of (17) is uncertain. The measurements of Moseley et al. (1970) lead to a thermal rate coefficient of $1.7 \times 10^{-7} (100/T)^{1/2} \text{ cm}^3 \text{ s}^{-1}$ whereas more recent experiments (Szucs et al. 1984, Peart, Bennett and Dolder (1985) are consistent with values nearer $7 \times 10^{-8} (100/T)^{1/2} \text{ cm}^3 \text{ s}^{-1}$ and close to the original theoretical predictions of Bates and Lewis (1955). The rate coefficient of (18) has not been determined but is probably of the order of $5 \times 10^{-7} (100/T)^{1/2} \text{ cm}^3 \text{ s}^{-1}$.

The importance of the isotopic molecule HD in cooling a hydrogen cloud was pointed out by Dalgarno and Wright (1972). The HD molecule is formed and destroyed by reactions similar to those which control the abundance of H_2 (Hirasawa 1969). In addition the HD molecule has a permanent dipole moment and can be formed by radiative association



Lepp and Shull (1984) have given an estimate of $10^{-25} \text{ cm}^3 \text{ s}^{-1}$ for the rate coefficient. The formation of HD may also be enhanced by the radiative association reactions



followed by



Of greater importance is the sequence

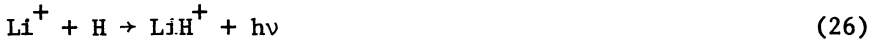


which is the main source of HD in diffuse interstellar clouds (Dalgarno, Weisheit and Black 1973, Black and Dalgarno 1973, O'Donnell and Watson 1974). Rate coefficients for (23) have been computed by Watson, Christensen and Deissler (1978) and for (24) have been measured by Fehsenfeld et al. (1973, 1974), Henchman, Adams and Smith (1981), and Smith, Adams and Alge (1982). Reactions (23) and (24) lead to a substantial fractionation of HD in the early Universe (Lepp, Dalgarno and Shull 1986).

Lepp and Shull (1984) draw attention to the possible importance of the less abundant molecule LiH, which they suggest could be formed by the radiative association process



with a rate coefficient of about $10^{-17} \text{ cm}^3 \text{ s}^{-1}$. Because lithium remains ionized to a lower radiation temperature than does hydrogen, the formation of the molecular ion LiH^+ by the radiative association of Li^+ and H,



may be more probable than the formation of LiH .

Thus the first objects were produced in an almost neutral atomic gas of hydrogen and helium with a fractional ionization of about 10^{-4} , a fractional molecular abundance of about 3×10^{-6} , and trace amounts of D, Li^+ , HD and LiH^+ . Those initial anisotropies embedded in the Universe whose masses exceeded the Jeans mass were unstable to gravitational collapse. They grew and formed collapsing pre-galactic clouds. The temperature of a cloud which collapses adiabatically varies as the two-thirds power of the density and the Jeans mass increases. If collapse is to continue, the gravitational energy released must be radiated away. The cooling of the cloud is brought about through the formation of molecular hydrogen which is enhanced through the reaction sequences involving H^+ ions and electrons as catalysts (Palla, Salpeter and Stahler 1983, Silk 1983, Lepp and Shull 1984). The fractional abundance of H_2 grew to 10^{-3} before the ionization was removed by recombination processes. The temperature rise was sufficient to suppress the initial enhanced abundance of HD relative to H_2 through the chemical exchange reactions



At densities exceeding 10^9 cm^{-3} , three-body recombination

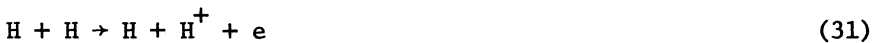


converted the remaining hydrogen to molecular form (Palla, Salpeter and Stahler 1983, Lepp, Dalgarno and Shull 1986). The temperature then rose slowly until the cloud became optically thick to the cooling radiation. Collision-induced dissociation of H_2 ,



(Yoshii and Sabano 1979) reduced the cloud to atomic form and briefly cooled the cloud before the temperature rise resumed.

The subsequent evolution depended on the efficiency with which the cloud became ionized. Palla, Salpeter and Stahler (1983) assumed that ionization occurred through direct impact



for which they adopted a rate coefficient of $9.9 \times 10^{-15} T^{1/2} \exp(-158,000/T) \text{ cm}^3 \text{ s}^{-1}$ (Drawin 1969). However both polar ionization



and associative ionization



are more favorable energetically with thresholds of respectively 12.87eV and 10.97eV. The rate coefficients of (32) and (33) are unknown.

Many of the original condensations may have terminated in explosions. In one model (Ostriker and Cowie 1981, Ikeuchi 1981), the explosive energy drives blast waves into the surrounding medium and sweeps up a supernova explosion in our galaxy (Bertschinger 1983, Vishniac, Ostriker and Bertschinger 1985). If the shell cools sufficiently, the gas can become gravitationally unstable and fragment into galaxies (Ostriker and Cowie 1981).

The formation of molecules in the cooling shocked gas may be crucial in determining the resulting galactic sizes (Wandel 1986). Detailed calculations of intergalactic shocks (Maclow and Shull 1986) indicate that H_2 is produced in the cooling shocked gas by the same chemical sequences that occurred in the recombination era and that the molecules can survive photodestruction by the background radiation from the galaxies that are formed.

The explosions may have injected heavy elements into the expanding Universe. Their presence in the shell material, though diluted by the primeval gas swept up by the blast wave, may enhance the cooling through the formation of hydrides by endothermic reactions such as



Whether or not the explosive amplification model is valid, it seems certain that molecular processes play a crucial role in galaxy formation as they do in star formation (cf. Silk 1985).

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DISCUSSION

GREENBERG: Would you anticipate that as a result of the early explosions after the first condensation, the expanding blast waves would have generated voids or bubbles within the shells of galaxy formation?

DALGARNO: Yes, though additional events may be necessary to produce the observed voids.

SHAPIRO: What relation, if any, does the Jeans mass distribution you showed have to the contemporary stellar mass distribution?

DALGARNO: Further study is required of the dynamics of the collapsing objects to determine the mass distribution of the fragments. The Jeans masses are minimum masses.

GOEL: Is there any evidence that LiH does exist in interstellar medium?

DALGARNO: No. Abundance will be low and may be destroyed later.

LANGER: Is the temperature really important in determining the collapse of the clouds because turbulence, rotation and magnetic field may dominate the pressure in retarding collapse?

DALGARNO: It will certainly effect the sizes of the initial condensations and the fragmentation. What magnetic fields have you in mind?

HARTQUIST: Even if magnetic field and turbulence are important for the support of primordial condensations, the temperature, which depends on the chemical composition, is important in determining the rates of many wave damping mechanisms. The total damping rate limits the amplitude of the turbulence and hence, the pressure parallel to field lines.

SOMERVILLE: In the formation of molecular hydrogen, do optically-allowed radiative association reactions involving excited-state hydrogen atoms play a significant role?

DALGARNO: The population of excited hydrogen atoms even allowing for self-absorption, appears to be too small though the rate coefficient for formation from a ground and excited state atom may be quite high.

MCNALLY: It was not clear to me what size of masses were involved in the first collapse - from your viewgraph masses no greater than $10^6 M_{\odot}$ were shown. Was the first collapse comprised of objects of sub-galactic masses?

DALGARNO: $10^6 M_{\odot}$ is probably the mass of the first fragment. Any perturbation giving a mass larger than $10^6 M_{\odot}$ is also unstable and will collapse. The distribution of masses will reflect the united spectrum of perturbation. However, fragmentation will likely begin with $10^6 M_{\odot}$, the size of globular clusters, and end with stellar sizes sizes $\sim 1 M_{\odot}$.

GREENBERG: In view of the formation of a significant number of heavy elements during the first explosive reaction, wouldn't you also expect some solid particle condensation (formation) along with the formation of galaxies so that even the first galaxies already contained some dust?

(addendum) Could the infrared rotation of this pregalactic (or proto-galactic) dust have played a role in the condensation of the galaxies?

DALGARNO: Some perhaps, but very little. (Same answer to the addendum).

NORMAN: You mentioned that in the explosions of the $10^5 \rightarrow 10^6 M_{\odot}$ objects, cosmic rays might be generated. Would you expect that such explosions would leave behind black holes, and if so, what might the masses of these black holes be?

DALGARNO: They will depend upon the pattern of fragments created during the collapse of the primary condensations. The first galaxies were formed from clouds much more massive than $10^6 M_{\odot}$ but fragmented into stellar-sized objects with a tendency to heavier stars, many of which exploded like supernovae.

MELNICK: Since you predict that infrared rotational lines of H_2 will be a major coolant of the gas at $z = 10^3$ or 10^4 , will these H_2 lines, once redshifted, result in a measurable background continuum emission at millimetre or centimetre wavelengths?

DALGARNO: I think not. The galaxies were formed at a redshift z of about 5. The redshifted lines would be in the spectral range between 10 and 20 μm .

VENUGOPAL: In the scenario of the formation of protogalaxies you presented, will it be possible to observe the 21 cm H-line redshifted? If so, what will be the order of antenna temperature expected?

DALGARNO: I think not. Negligible.

LEGER: Does your model of population III stars have any predictions that could be tested but the mere existence of galaxies? (Nucleosynthesis, Cosmic Ray production....)

DALGARNO: There should be diagnostic tests once the consequences have been properly evaluated. Your suggestions are two of the possibilities.