STELLAR ATMOSPHERES:
THE SOURCES OF INTERSTELLAR MOLECULES

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Abstract. The analysis of the abundance of interstellar molecules in compact H II regions suggests that the molecules are formed in stellar atmospheres (possibly of protostars or of late type stars), transported to the location of the neutral clouds in the cpmpact H II regions, and shielded from decomposition due to stellar radiation by the dust in the clouds. Cometary nuclei and interstellar dust are argued from the astrochemical point of view to be dirty ice of the second kind (or a sort of frozen interstellar molecules). The chemical structure of the primordial solar nebula is discussed under the assumption that long-period comets consist of the most primordial substances of the solar system.

1. Introduction

Recently more than twenty kinds of interstellar molecules have been found by radio-astronomers in the compact H II regions of our galaxy. Emission lines from more than thirty kinds of molecules have been searched for but have not been detected. A careful survey on the physico-chemical character of each molecule might suggest the formation mechanisms of these molecules.

One of the most conspicuous feature of the interstellar molecules in the compact H II regions is that CO is so plenty as to contain almost all the C atoms in the neutral clouds in these regions. Furthermore, N atoms in the same clouds appear to be in the form of N_2 (which is difficult to be found in the radio wave region), because the amount of all the other detected nitrogen compounds such as CN, HCN, NH_3 etc. are very much smaller than the total amount of N atoms expected in these clouds from the 'cosmic abundance'. CO and N_2 are stable molecules at high temperature, say at 1500–4500 K (see Figure 1). This evidence suggests that interstellar molecules were formed in the stellar atmospheres. Excess of O atoms might form OH and H_2O at these temperatures. If the interstellar moleucles are formed on the dust grains in the neutral clouds, the most natural products under the conditions of low temperature (70–100 K) and of hydrogen rich environment might be CH_4 and NH_3, contrary to the above observational evidence.

It is easily found that the composition of cometary atmosphere resembles the abundance distribution of interstellar molecules in the compact H II regions: Even from the results disclosed *until present*, we know that OAO 2 has detected two kinds of new chemical species, H and OH, which might be expected in the compact H II region, at least in the form of H_2O. Emission bands of N_2^+ and CO^+ were already found in cometary tails. Some molecules found at optical wavelengths, such as C_2, CN, CH, NH, etc., may merely be the minor constituents of the cometary atmospheres. This evidence suggests that cometary nuclei were essentially frozen interstellar mole-

Greenberg and Van de Hulst (eds.), Interstellar Dust and Related Topics, 405–412.

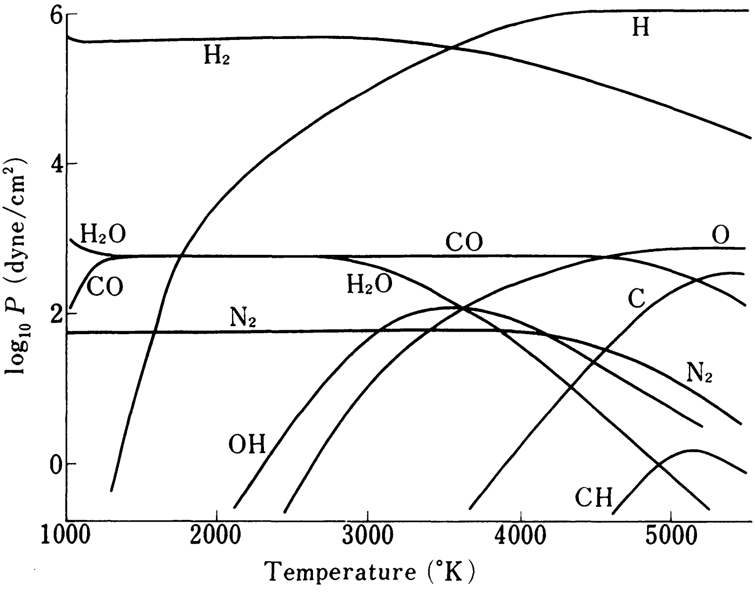

Fig. 1. Some examples of the abundances of various molecules at the temperatures of 1000–5500 K and at the pressure of 10^6 dyn cm^{-2}.

cules or 'dirty ice of the second kind' (the composition is H_2, CO, N_2, OH, H_2O, and some atoms, with some silicates and metallic compounds), in contrast to 'dirty ice of the first kind' (the composition is H_2O, CH_4, and NH_3 with some condensates) so far assumed.

Comets may be formed in the primordial solar nebula in the vicinity of Jovian orbit and be scattered to the present cometary reservoir at the fringe of the solar system by the perturbation of stars and giant planets (Oort, 1950). Or, they may be trapped from the interstellar space by the gravity of the Sun (Lyttleton, 1948). In these cases, the possible sources of cometary molecules may be the atmospheres of the protosun (more generally the prestellar atmospheres) and the atmospheres of late type stars, respectively, since these stars have some favorable properties for the ejection of molecules from their atmospheres to the dusty circumstellar envelopes, such as low temperature, high convection, and small gravities.

2. Abundances of Interstellar Molecules

At the high temperature such as that of stellar atmospheres, thermochemical equilibrium may easily be established. The advantage of thermochemical calculation is that it uses a few parameters, essentially temperature and pressure, to discuss the abundances of many kinds of molecules. We have calculated the abundances of molecules, including H, C, N, O, S, P, and Si atoms in them, at the temperature of 1000–6000 K and at the pressure of about 1 atm. After an averaging procedure over the mass distribution of stars in a galactic cluster, the calculated distributions were found to be in good agreement with the observed abundances (Shimizu, 1973). Here we shall refer to only a few examples which are necessary for the discussions in the following sections or the recent results that we have discussed in this symposium.

(1) Minor constituents of cometary atmospheres such as C_2, CN, NH, CH etc. are most stable at around 4000–5000 K, the effective temperature of the protosun (Narita *et al.*, 1970). At this temperature, the amounts of atoms are comparable with those of molecules. The presence of O atoms in the cometary coma were confirmed by the detection of its emission line at 6300 Å. A part of the O atoms may be in the photodissociation product of H_2O but some of them may be contained in the cometary nuclei from the beginning.

(2) The observed amount of recently detected H_2S in the compact H II regions is comparable with that of CS (P. Thaddeus, private communication), and is in a good agreement with the result of our calculation, again at the temperature of 4000 K. PN could not be observed with the sensitivity such that, if all P atoms are contained in the molecule, it should be detected (B. E. Turner, private communication). This may be due to the instability of this molecule at high temperature, contrary to N_2, because of its relatively small dissociation energy.

(3) In his review on interstellar molecules at this symposium Snyder suggested that Xogen at 89 GHz might be C_2H. This is very likely from our standpoint, because the dissociation energy in the C_2-H bond is 5.7 eV, much larger as compared with that of the usual C – H bond, 3–4 eV. The detailed calculation of its abundance is not possible

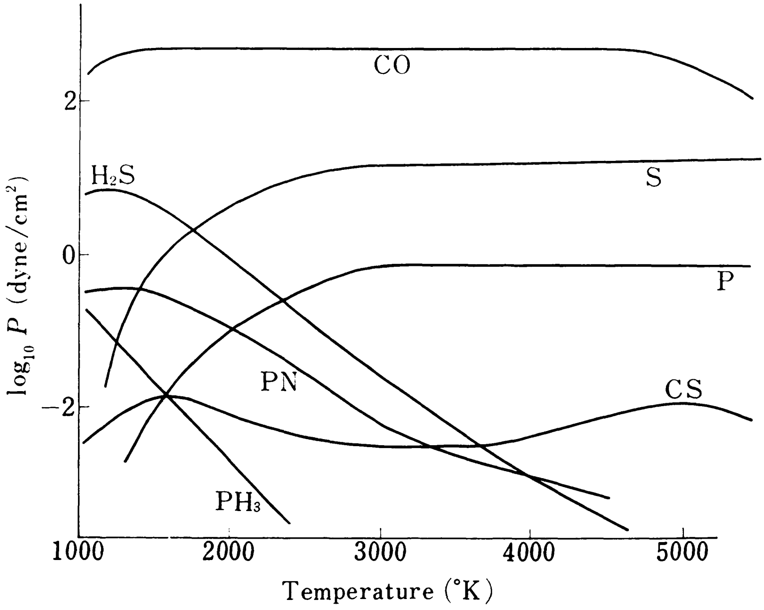

Fig. 2. Some examples of the abundances of the molecules including S and P at the temperatures of 1000–5500 K and at the pressure of 10^6 dyn cm^{-2}.

at present because of the lack of some molecular data of this molecule. A rough estimation by taking into account the dissociation energy only gives a rather large abundance of C_2H, say comparable with that of C_2, at the temperature of 4000 K. HC_3N is composed of C_2H and CN. Therefore, if the amount of C_2H is plenty, that of HC_3N might also be abundant. Furthermore, the bond between these radicals are stabilized by the resonance phenomenon called hyperconjugation between the two triple bonds in C_2H and CN (Mulliken, 1939). A rough thermochemical equilibrium estimate again gives a rather large amount of this molecule. The actual existence of HC_3N, a rather complex molecule, in many compact H II regions was reported by Morris *et al.* (1973).

3. Protostar Theory

One of the candidates for the location of molecular formation whose physical condition may be adequate for the ejection of interstellar molecules is the prestellar atmosphere, because recent theoretical studies on protostars suggest that they have very large radii and wholly convective atmospheres. An explanation of the similarity between interstellar molecules and cometary atmosphere might be that interstellar molecules ejected from the protosun were accreted to be comets in a very cool region of the solar nebula where the sunlight was completely shielded by the dense dust around the protosun. If the accreted mass could grow up to that of planets, the heat of accretion would have changed the composition of the molecules. Such a possibility seems to explain the fact that the present atmospheres of Jovian planets contains H_2, CH_4, and NH_3 in accord with their effective temperatures. On the other hand, comets scattered to the fringe of the solar system may keep their initial composition.

The reported mass loss in the form of neutral molecules from IRC + 10216 and red giants whose physical conditions are rather similar to that of protostars might suggest the possibility of neutral mass ejection from the protostar. If a protostar pulsates, there might be a chance of the instability in the prestellar atmosphere to eject the neutral molecules. Such a pulsation phenomenon might correlate with the Titius-Bodes' law in the solar system: According to Weizsäcker (1944), this law may well be explained by assuming a turbulence in the solar nebula, with a regular system of vortices whose number in the orbits of the planets should be 5. If the protosun pulsated, the hydrodynamical tide occurred in the vicinity of the sun might propagate in the solar nebula and dissipate in it by the interaction with the differential rotation of the nebula to form turbulence. This is not the free mixing of the nebula so far discussed (ter Haar, 1950), but forced mixing. Consequently the turbulence may continue much longer than the free mixing time, 10^3 yr. The above magic number, 5, might be explained in discussing the dispersion relation of the nebular waves. This point will be argued in another paper.

In relation to this argument, it is noteworthy that Herbig (1970) already discussed a possiblity for the formation mechanism of interstellar dust that they were blown off from the 'solar' nebula by the pressure of radiation and particles of the very young 'Sun'.

4. Late Type Star Theory

As suggested in the introduction, it may also be possible to explain the similarity of interstellar molecules with cometary atmospheres by the formation of molecules in the atmospheres of the late type stars. There is no spatial correlation of late type stars with compact H II regions. Consequently the molecules should be sufficiently shielded by some means from decomposition by the stellar ultraviolet radiation in the interstellar space during the transport from the stars to the dustry neutral clouds in the compact H II regions. This might be possible if the molecules are frozen in a sufficiently large lump which absorbs and scatters the stellar radiation at the surface.

There is some evidence that the neutral molecules are ejected from some kinds of late type stars, as we have seen in the previous section. Comets might be formed in the envelopes of these stars by a similar mechanism to that in the solar nebula. (The number of comets in our solar system is said to be decreasing during 4.5 b.y. though their loss to the interstellar space by planetary perturbation or through their decomposition in the vicinity of the Sun. If the supply of comets from the interstellar space is necessary to explain their present number, there should be places of cometary formation somewhere in our Galaxy.) According to this theory, interstellar dust is formed in the envelopes of late type stars and its composition is again dirty ice of second kind.

Witkowski (1970) suggested the possibility that the number of comets in our Galaxy was 0.5×10^{23} in his discussion of the origin of the comets. Then the total mass of comets may be comparable with that of fine interstellar dust grains in the Galaxy. Dust of intermediate mass between the micron-size dust and comets might also exist in interstellar space. A lot of such large-size dust grains may be contained in the dark neutral clouds and be melted to be observable in the form of molecules by the heat of protostars or of the shock waves accompanied with the gravitational collapse of the clouds.

5. Dirty Ice of the Second Kind and the Primordial Solar Nebula

In this section we shall attempt to explain some chemical features of cosmic dust, comets, and planets in terms of dirty ice of the second kind defined in the first section.

It is known that the life times of possible parent molecules of the radicals in the cometary coma estimated from the laboratory measurements of absorption cross-section and the observed solar ultraviolet flux are too large to explain the observed life times (Potter and Del Duca, 1964). One of the possibility to avoid this difficulty is to assume that radicals are contained in the cometary nucleus from the beginning and are evaporated by the heat of the sunlight at the fringe of an icy halo surrounding the nucleus (Delsemme and Wenger, 1970). The evaporation of dirty ice of the second kind easily produces an atmosphere similar to comets. The radical reactions in the nuclei might provide free energy for cometary bursts (Donn and Urey, 1956). If cometary atmospheres contained a great amount of H_2 and H, the main ions around the comet would be H^+ instead of CO^+ and N_2^+. Then the ion density in the cometary ionosphere

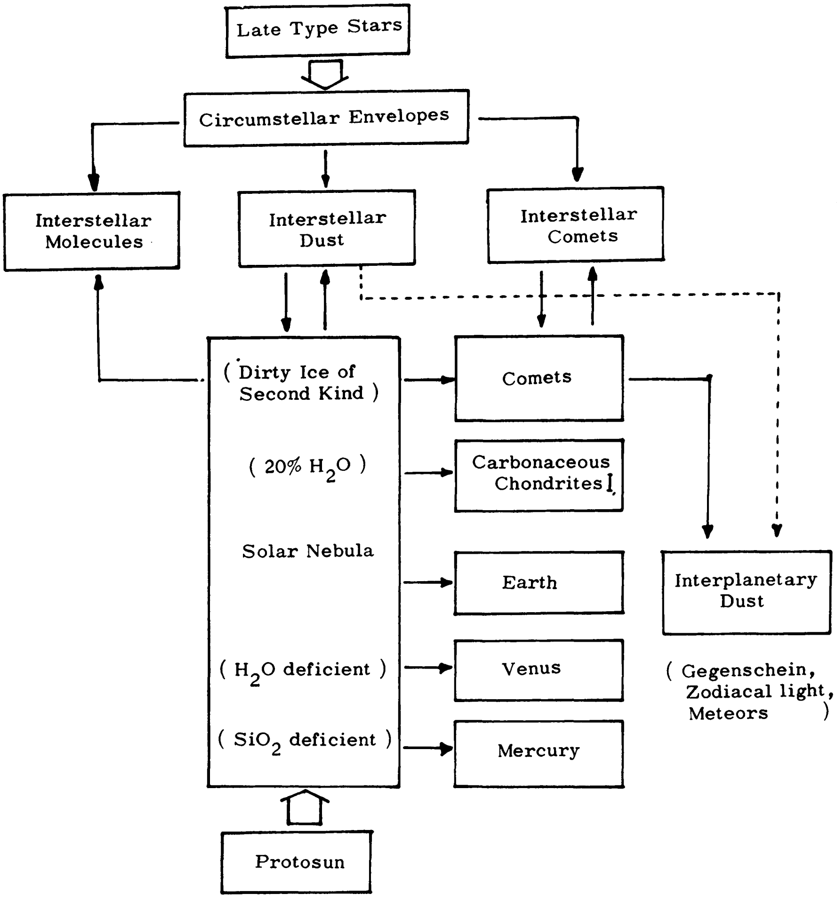

Fig. 3. A possible flow diagram among the highly convective stars, planets, dust, and molecules

should be large, due to the slow recombination rate of this atomic ions with electrons. Such a situation is similar to the case of the Jovian ionosphere (Shimizu, 1971).

The origin of interplanetary dust in the vicinity of the Earth is frequently ascribed to the debris of comets. The volatiles in it may evaporate due to the heat of the Sun and only metals and silicates may remain in the dust after a long time. Dust in the cometary tails might also be the same kind of substances.

Recently it was suggested that the chondrites were formed by the direct accretion of the substances in the primordial solar nebula (Anders, 1971). Under the assumption that the dirty ice of the second kind chemically represents the dust at the outer part of the solar nebula, we may obtain the following working hypothesis for the chemical structure of the solar nebula:. The primordial solar nebula was so opaque due to the dust in it that the intensity of solar radiation decreased according to an exponential law, instead of a r^{-2} law, before the accretion time. Mercury may have been formed by the accretion of dust which was deficient of volatile substances and even deficient of a part of the silicates due to the strong irradiation from the primordial Sun at its very active phase with the luminosity of 10 $L_\odot$ (Narita *et al.*, 1970). At the orbit of Venus, the solar radiation was still strong enough to evaporate most of the H_2O in the dust. (Sometimes the scantiness of H_2O on Venus is acribed to the escape of H from its exosphere after the photodissociation of H_2O. However, the accumulation of O_3 in the lower atmosphere should form a cold trap for H_2O which prevented the transport of water from the lower atmosphere to the photochemical level, as discussed by Berkner and Marshall (1965) in the case of the Earth.) There is a possibility that a fair part of the solar radiation was absorbed between Venus and the Earth. If Venus were ground into fine dust and put close together at its orbit, the thickness of the dust may roughly be estimated to be of the order of cm, which may be enough to absorb the solar radiation to keep some amount of water to form ocean on the Earth later, in the dust at 1 AU from the sun. Type I carbonaceous chondrites which contain 20% of water might be accreted at more distant location and comets might be formed in the completely dark nebula (Figure 3).

It should be remarked that the above suggestions have been obtained from the astrochemical consideration only. Details on the physical properties of the primordial solar nebula will be studied in the future.

6. Conclusions

It is found from a thermochemical calculation that interstellar molecules may be formed at places of high temperature and of high pressure. Such a physical condition is quite different from those in cool and tenuous interstellar space. Molecules may be formed in the atmospheres of some stars, possibly protostars and/or late type stars, transported to the dusty clouds in the compact H II regions by some means, and may survive there for a time long enough to be observable. If the interstellar molecules are formed around late type stars, the existence of a lot of cometary substances in the interstellar space and an exchange of matter between the solar system and interstellar space follows.

In the cool and dark regions of the solar nebula, the molecular condensates may be put close together to form comets consisted of dirty ice of second kind by some mechanism similar to the formation mechanism of planetesimals of the Jovian planets. The solar nebula in the vicinity of the protosun may be deficient of volatiles due to the high luminosity of the Sun (Narita *et al.*, 1970). This nebular model might explain the sucessive chemical properties in the Mercury-Venus-Earth-carbonaceous chondrites-comets sequence. Interstellar dust could also be the dirty ice of the second kind.

The above discussion might suggest that long-period comets were the most primordial substances in the solar system and that good clues for studying the origin of the solar system would be obtained from the new observation of comets at ultraviolet, far-infrared, and radio wavelengths by the space probes in the near future.

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