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FORMATION OF INTERSTELLAR MOLECULES ON THE SURFACE OF GRAINS

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Relative amounts of molecules formed by relaxation type reactions between radicals(atoms) and radicals(atoms) on the grain surfaces are calculated. The result can explain the formation mechanism of observed molecules. A prediction has been made on molecules such as methylamine which are expected to be detectable.

Recently many complex molecules have been discovered in interstellar space.[1] These are listed in Table 1. The formation mechanism of simple molecules are studied by many authors.[2~9]

TABLE 1 DISCOVERED MOLECULES AND RADICALS

Saturated	Double Bond	Triple Bond	Radical
H_2	HCHO	HCN	OH
NH_3	HCOOH	HCCCN	CN
H_2O	NH_2CHO	CH_3CN	CH
CH_3OH	OCS	HNC	
H_2S	CH_2NH	CH_3CCH	
	HCHS	CO	(SiO)
	CH_2CO		(CS)
	CH_3CHO		

Watson and Salpeter have considered reactions between radicals and molecules such as $NH_3 + CH_2 = HCN + 2H_2$ and $HCHO + HCHO = CH_3COOH$ on the surface of grains.[10][11] Their assumption of molecules as reactants has serious difficulties that reactant "molecules" must be adsorbed on the surface, but product "molecules" must be evaporated from the surface.

At low temperature of 5°~10°K on the interstellar grain, the reaction supposed by them are difficult to occur without photo-excitation. Besides, they could not explain the variety of discovered molecules.

We consider a following mechanism. Atoms fall onto a grain surface continu-

ously and are adsorbed. These atoms react to form radicals. Atoms and radicals adsorbed on a grain surface react with each other by an encounter without activation energy until molecules are formed. Molecules can evaporate to the space at a time of formation, while radicals remain on the surface. Radicals such as OH and CN were observed and their formation will be explained with other than above mechanism. As the abundance of these radicals are supposed to be extremely low in comparison with those of atoms in interstellar space, these radicals are not considered in our mechanism. We have calculated the relative amounts of formed molecules on the basis of following postulations; (1) 64 radicals and 58 molecules are supposed, which consist of H, C, O and N and have four heavy atoms at most. (2) The rate-constants of the reactions between radicals and atoms on the grain surface are the same. (3) The formation rates of molecules depend on radical and atom concentration on the grain surface. (4) The ratio {H} / {C,O,N} is to be 1000,100,10 and 1. The first value represents approximately the cosmic abundance and the latters low concentrations of hydrogen atoms due to existence of H_2 molecules and low sticking tendency of H atoms onto the grain surface.

The calculation are done with following equations, for atoms, such as d[H]/dt = {H} - k[H][A & R], for radicals, such as d[CHO]/dt = k([O][CH] + [C][OH] - [CHO][A & R]) and for molecules, such as d(HNCO)/dt = k([H][NCO] + [N][HCO] + [OH][CN]). [ ] denotes the concentration of atoms and radicals on the grain surface, { } the number of following atoms onto a grain per unit area and unit time, ( ) the number of molecules evaporating from a grain per unit area and [A & R] the concentrations of the atoms and radicals with which the concerned atoms or radicals react to form molecules. Table 2 shows the result of numerical solution through above equations. Comparing the result of calculations with the observation : (1) High yields are predicted for discovered molecules. (2) The discovery of molecules which have N-O, N-N and O-O bonds are expected. (3) With decreasing R, amounts of the molecules which have many heavy atoms increase.

Table 3 lists the molecules which have: (1) dipole moment and (2) faster rates of predicted molecules than " the slowest one among observed molecules". We expect that such molecules can be detected. Although in our calculations there are many molecules which have the bonds of N-O, N-N and O-O, they are not discovered hitherto. On the grain surface there may be a special kind of interaction, like as hydrogen bonding, which restricts the behavior of N and O atoms.

TABLE 2 AMOUNTS OF FORMED MOLECULES

The quantities are normalized on the basis of CO amount as unit and represented logarithmically.

P={H}/{C,O,N} Molecule	1000	100	10	1		1000	100	10	1
H_2(obs.)	5.99	3.99	1.99	$\bar{1}$.98	HNO_2(n.o.)	$\bar{3}$.43	$\bar{2}$.38	$\bar{1}$.03	$\bar{2}$.89
H_2O(obs.)	2.99	1.96	0.79	$\bar{1}$.33	$HNCHNH_2$(n.o.)	$\bar{3}$.33	$\bar{2}$.21	$\bar{2}$.37	$\bar{4}$.52
NH_3(obs.)	2.95	1.90	0.57	$\bar{2}$.47	CH_3CHCH_2(n.o.)	$\bar{3}$.30	$\bar{2}$.15	$\bar{2}$.07	$\bar{5}$.31
CH_4(imp.)	2.88	1.81	0.33	$\bar{3}$.60	HCCCN(obs.)	$\bar{4}$.98	$\bar{3}$.97	$\bar{2}$.81	$\bar{2}$.93
CH_2NH(obs.)	0.69	0.61	0.07	$\bar{2}$.39	CH_3CH_2OH(n.o.)	$\bar{3}$.01	$\bar{3}$.86	$\bar{3}$.81	$\bar{5}$.24
N_2(imp.)	0.58	0.55	0.40	0.11	$CH_3CH_2NH_2$(n.o.)	$\bar{4}$.66	$\bar{3}$.50	$\bar{3}$.40	$\bar{6}$.40
NH_2OH(n.o.)	0.60	0.53	0.03	$\bar{2}$.29	CH_2CHCN(n.o.)	$\bar{5}$.29	$\bar{3}$.18	$\bar{2}$.41	$\bar{3}$.39
HCHO(obs.)	0.56	0.52	0.20	$\bar{1}$.09	H_2CCCO(n.o.)	$\bar{5}$.25	$\bar{3}$.15	$\bar{2}$.51	$\bar{2}$.17
HCCH(imp.)	0.56	0.51	0.15	$\bar{1}$.05	HCCCCH(imp.)	$\bar{5}$.21	$\bar{3}$.11	$\bar{2}$.46	$\bar{2}$.13
HCN,HNC(obs.)	0.47	0.44	0.28	$\bar{1}$.73	NCCHO(n.o.)	$\bar{5}$.14	$\bar{3}$.06	$\bar{2}$.56	0.85
CH_2CH_2(imp.)	0.45	0.36	$\bar{1}$.70	$\bar{3}$.40	$(CHO)_2$(n.o.)	$\bar{5}$.13	$\bar{3}$.03	$\bar{2}$.38	$\bar{2}$.12
HOOH(n.o.)	0.27	0.21	$\bar{1}$.86	$\bar{2}$.77	$CH_2(OH)CN$(n.o.)	$\bar{5}$.06	$\bar{4}$.95	$\bar{2}$.16	$\bar{3}$.22
CH_3OH(obs.)	0.30	0.21	$\bar{1}$.57	$\bar{3}$.23	CH_3NHCHO(n.o.)	$\bar{5}$.08	$\bar{4}$.93	$\bar{3}$.85	$\bar{5}$.78
NH_2NH_2(n.o.)	0.18	0.09	$\bar{1}$.41	$\bar{3}$.13	CH_2CHCHO(n.o.)	$\bar{5}$.03	$\bar{4}$.90	$\bar{3}$.97	$\bar{4}$.42
NO(n.o.)	0.004	0.03	0.07	$\bar{1}$.97	CH_2CCCH_2(imp.)	$\bar{6}$.98	$\bar{4}$.85	$\bar{3}$.91	$\bar{4}$.35
CO(obs.)	0.00	0.00	0.00	0.00	CH_3CH_2CN(n.o.)	$\bar{6}$.99	$\bar{4}$.85	$\bar{3}$.77	$\bar{5}$.87
O_2(imp.)	$\bar{1}$.99	$\bar{1}$.99	$\bar{1}$.98	$\bar{1}$.94	CH_3NO_2(n.o.)	$\bar{6}$.90	$\bar{4}$.78	$\bar{3}$.92	$\bar{3}$.01
CH_3NH_2(n.o.)	0.09	$\bar{1}$.97	$\bar{1}$.18	$\bar{4}$.26	$CH_2CHCHCH_2$(imp.)	$\bar{6}$.77	$\bar{4}$.60	$\bar{3}$.38	$\bar{6}$.57
CH_3CH_3(imp.)	$\bar{1}$.80	$\bar{1}$.67	$\bar{2}$.81	$\bar{5}$.95	CH_3CHCHO(n.o.)	$\bar{6}$.73	$\bar{4}$.56	$\bar{3}$.36	$\bar{6}$.54
NH_2CHO(obs.)	$\bar{2}$.18	$\bar{1}$.09	$\bar{1}$.44	$\bar{2}$.11	NH_2CONH_2(n.o.)	$\bar{6}$.65	$\bar{4}$.53	$\bar{3}$.64	$\bar{5}$.96
CH_3CN(obs.)	$\bar{2}$.13	$\bar{1}$.04	$\bar{1}$.39	$\bar{2}$.04	$CH_3CH_2CH_3$(imp.)	$\bar{5}$.67	$\bar{4}$.53	$\bar{4}$.61	$\bar{7}$.44
H_2CCO(obs.)	$\bar{3}$.91	$\bar{2}$.84	$\bar{1}$.34	$\bar{2}$.64	NCCN(imp.)	$\bar{6}$.56	$\bar{4}$.51	$\bar{2}$.15	$\bar{1}$.02
CH_3CCH(obs.)	$\bar{3}$.92	$\bar{2}$.81	$\bar{1}$.05	$\bar{3}$.03	$CH_2(OH)CHO$(n.o.)	$\bar{6}$.36	$\bar{4}$.23	$\bar{3}$.28	$\bar{5}$.82
CH_3CHO(obs.)	$\bar{3}$.83	$\bar{2}$.72	$\bar{2}$.94	$\bar{4}$.99	$H_2NCHCHNH_2$(n.o.)	$\bar{6}$.36	$\bar{4}$.20	$\bar{3}$.02	$\bar{6}$.50
HNCO,HOCN(obs.)	$\bar{3}$.74	$\bar{2}$.68	$\bar{1}$.33	$\bar{1}$.22	H_2NNO(n.o.)	$\bar{7}$.24	$\bar{4}$.14	$\bar{3}$.43	$\bar{2}$.30
HCOOH(obs.)	$\bar{3}$.62	$\bar{2}$.55	$\bar{1}$.05	$\bar{2}$.37	H_2NCCNH_2(n.o.)	$\bar{6}$.23	$\bar{4}$.11	$\bar{3}$.30	$\bar{5}$.95
CH_2CHNH_2(n.o.)	$\bar{3}$.66	$\bar{2}$.54	$\bar{2}$.67	$\bar{4}$.42	CO_2(imp.)	$\bar{6}$.17	$\bar{4}$.08	$\bar{3}$.42	$\bar{3}$.16
$NCNH_2$(n.o.)	$\bar{3}$.61	$\bar{2}$.54	$\bar{1}$.03	$\bar{2}$.31	CH_3COOH(n.o.)	$\bar{6}$.06	$\bar{5}$.92	$\bar{4}$.97	$\bar{5}$.47
HNO(n.o.)	$\bar{3}$.48	$\bar{2}$.39	$\bar{2}$.76	$\bar{3}$.57	$CH_3CHCHNH_2$(n.o.)	$\bar{6}$.01	$\bar{5}$.84	$\bar{4}$.66	$\bar{6}$.08

(obs.) : observed. (n.o.) : not observed. (imp.) : with no dipole moment.

Accordingly, the existence of these molecules have to be examined from other point of view. Methyl amine should be discovered in future certainly, because it has no these bonds.

Interstellar molecules dissociate by the action of u.v. light from surrounding stars. We calculated the rate of photo-dissociation in various types of clouds. Using this rate and the result of Table 2, we calculated the abundance of several molecules.

There are reliable observed data for CO and HCHO in the constellation of Sagittarius and in one of Orion.[1] The observed ratio of CO/HCHO is $10^4 \sim 10^5$ which is in good agreement with the present calculation.

Details of this argument will be given in forthcoming papers.

TABLE 3 THE MOLECULE EXPECTED TO BE DISCOVERED

R={H}/{C,O,N} Sequence of Abundance	1000	100	10	1
1	H_2NOH	H_2NOH	NO	NO
2	HOOH	HOOH	H_2NOH	HNO_2
3	H_2NNH_2	H_2NNH_2	HOOH	NCCHO
4	NO	NO	H_2NNH_2	HOOH
5	CH_3NH_2	CH_3NH_2	CH_3NH_2	NH_2OH
6	CH_2CHNH_2	CH_2CHNH_2	$NCNH_2$	HCCCNO
7	$NCNH_2$	$NCNH_2$	HNO_2	HCCCNO
8	HNO	HNO		$(CHO)_2$
9	HNO_2	HNO_2		CH_3NO_2
10	$HNCHNH_2$	$HNCHNH_2$		HNO
11	CH_3CHCH_2	CH_3CHCH_2		H_2CCHCN
12				$NCNH_2$
13				$NCCH_2OH$
14				H_2NNH_2

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