Deuterium fractionation of methylamine through atomic grain-surface reactions at low temperatures: implication for the possible D/H ratio in molecular clouds

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Interstellar methylamine (CH_3NH_2) was first found in 1974 toward Sgr B2 and Ori A [1]. This finding is of interest in view of astrobiology because methylamine could be a precursor of amino acid in space [2]. Laboratory studies revealed that methylamine can be formed by various reactions both in the gas phase and the solid phase in molecular clouds (MCs) [3,4]. In either case, it is likely that the CH_3NH_2 is retained on icy grains at as low as 10 K and is subjected to various processes on them.

Deuterium (D) fractionation of interstellar molecules is an important issue when considering chemical evolution in MCs. Previous studies revealed that atomic grain-surface reactions play a significant role for the D enrichment of interstellar molecules such as CH_3OH [5] and H_2CO [6]. Although D-substituted methylamine has never been observed, it is reasonable to consider that interstellar methylamine is deuterated to some extent. In the present study, we performed laboratory experiments on the hydrogen (H)-D and D-H substitution reactions of solid methylamine through atomic-surface reactions at low temperatures. Based on the obtained experimental results, we estimated a possible D/H ratio of methylamine brought by atomic-surface reactions in MCs.

When solid CH_3NH_2 was exposed to D atoms at 10 K, deuterated methylamine CD_3ND_2 was produced. Then we measured the rate of the H-D substitution at the functional group level by using partly deuterated methylamines CD_3NH_2 and CH_3ND_2; the H-D substitution rate of methyl group was about 10 times larger than that of amino group and on the same order with that of methanol [5]. When deuterated methylamine CD_3ND_2 was exposed to H atoms at 10 K, hydrogenated methylamine CH_3NH_2 was produced. D-H substitution rate of methylamine was also measured at the functional group level: 0.4 for the methyl group and 0.1 for the amino group relative to the H-D substitution rate of methyl group.

Based on the measured H-D and D-H substitution rates of methylamine, we calculated time-variations in the fractional abundances of methylamine isotopologues brought by atomic surface reactions in MCs. Assuming that only CH_3NH_2 is present at time $t = 0$, atomic D/H = 0.01, and $n(\mathrm{H}) = 1\ \mathrm{cm}^{-3}$, about 3% of CH_3NH_2 is converted into deuterated methylamines at $t = 10^6$ years where the typical lifetime of MCs. Among deuterated methylamines, CH_2DNH_2 is the most abundant, followed by CH_3NHD. The singly-deuterated methylamines comprise about 97% of total deuterated methylamines.

The present study proposes that deuterated methylamines are possibly present in MCs, although their absolute abundances may not be large. Future astronomical observations with better S/N are highly desired for the detection of deuterated methylamines.

References

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