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Theoretical Studies of the Chemical Processes of Producing Methylamine and Methanol in the Interstellar Space

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A hypothesis for the mechanism forming CH_3NH_2 and CH_3OH in interstellar space is examined with the ab initio MO calculations. In the hypothesis, both of CH_3NH_2 and CH_3OH are assumed to be formed via two steps, radiative association reaction and dissociative recombination reaction. The calculations support the possibility of the two-step mechanism for CH_3OH, but the first step radiative association reaction for CH_3NH_2 is proved to be unfavorable. Based on the calculational results, an alternative reaction mechanism is proposed.

Nearly a hundred molecules and molecular ions are identified in the interstellar clouds by the observation of the electromagnetic wave from the universe with the radio telescope and by the molecular spectroscopy in the laboratory. Methylamine CH_3NH_2 and methanol CH_3OH are among the list of the observed interstellar molecules, and they are the key molecules of synthesizing larger organic molecules in the interstellar clouds.[1—8] But the forming mechanism of CH_3NH_2 and CH_3OH in the interstellar space is not understood.

Interstellar molecules are formed under low temperature, low density, and nonequilibrium conditions. The ternary collision reaction and endothermic reaction that can be observed easily in the laboratory cannot proceed in the interstellar clouds. The processes to form the molecules must not need activation energies. Besides, they must have the means to remove the surplus heat of reactions.

Herbst suggests in his review article[1)] that CH_3NH_2 is formed by radiative association reaction of CH_3^+ (which has not been observed in interstellar space) and NH_3 (which has been observed) [Eq. 1] followed by dissociative recombination [Eq. 2]

$$CH_3^+ + NH_3 \rightarrow CH_3NH_3^+ + h\nu, \tag{1}$$

$$CH_3NH_3^+ + e \rightarrow CH_3NH_2 + H. \tag{2}$$

He also suggests that CH_3OH is similarly formed by a two-step mechanism, radiative association reaction of CH_3^+ and H_2O (which has been observed) [Eq. 3] and dissociative recombination [Eq. 4],

$$CH_3^+ + H_2O \rightarrow CH_3OH_2^+ + h\nu, \tag{3}$$

$$CH_3OH_2^+ + e \rightarrow CH_3OH + H. \tag{4}$$

In this paper we examine the above hypothesis with the ab initio calculations. We found that these two molecules are formed via different reactions; methanol can be formed via the reactions of Herbst's hypothesis, but not methylamine. An alternative forming mechanism is proposed for methylamine.

Computational Methods

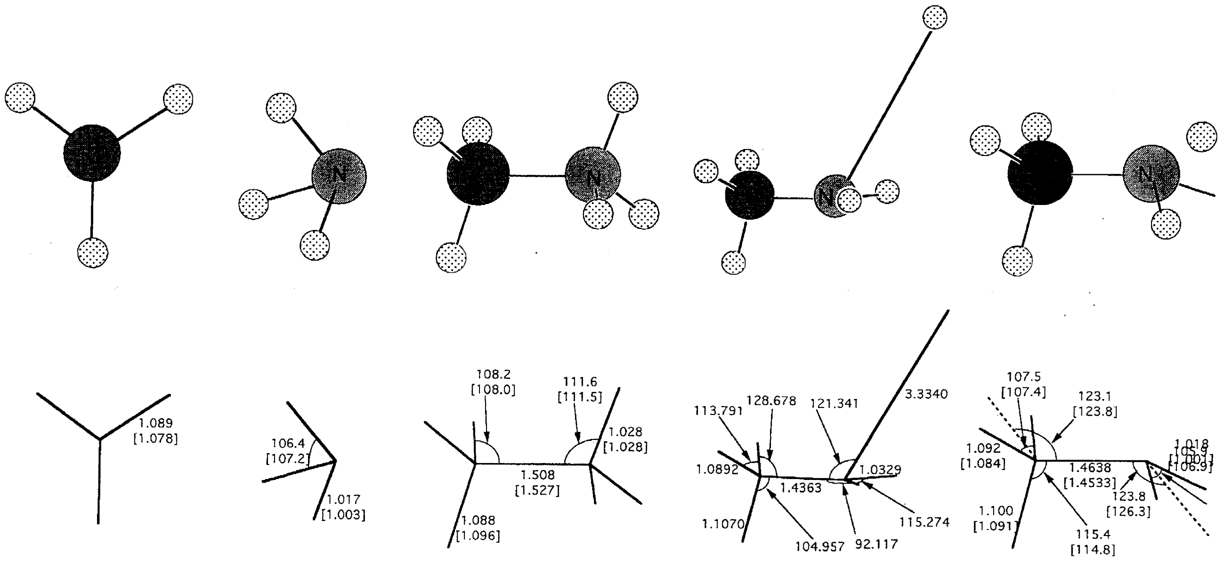
To confirm whether the reactions can proceed or not, we first optimize geometries and evaluate the total energies for the reactants, products, and intermediates using unrestricted Hartree–Fock (UHF) and second and forth order Møller–Plesset (MP2, MP4) methods with the 6-31G* basis sets; The energy calculations in MP4 are performed while employing the structures of the results of MP2 calculations. The reaction paths and the transition state structure are searched with these methods and with Generalized Valence Bond (GVB) method. To draw the potential energy curves of the reactions, we make the distances between two reactants shorter or longer step by step by fixing the distance and optimizing the other structural parameters. For the doublet states examined, S^2 values are confirmed to be less than 0.765, and the spin contamination is small.

At the optimized structures, the energies are evaluated with the 6-311G(d, p) basis set; the energies evaluated with the larger basis set are given in the parentheses ( ).

All calculations were carried out using the Gaussian 86 and Gaussian 92 program package at the computer center at the Institute for Molecular Science.

Results and Discussion

Methylamine CH_3NH_2. At first, we optimized the geometric structures for the reactants and products of the reactions (1) and (2) and evaluated their total energies. The calculated geometric parameters are shown in Fig. 1. They are in good agreement with the published data,[9—15)] and some are slightly longer by 0.02 Å.



CH_3^+(D3h) E= -39.32943

NH_3(C3v) E= -56.35738

$CH_3NH_3^+$(C3v) E= -95.87617

$CH_3NH_2^+\cdots H$(Cs) E= -95.65869

CH_3NH_2(Cs) E= -95.51444

Fig. 1. Optimized geometries and total energies of the reactants and products of the reactions Eqs. 1 and 2 in MP2 level. Bond lengths in angstroms, angles in degrees, and energies in hartree.

The dissociative recombination reaction such as Eq. 2 is almost always energetically possible, though it is not easy to estimate the branching ratio among various possibilities of breaking bonds. In the present case, there are two other bonds to be broken:

$$CH_3NH_3^+ + e \rightarrow CH_2NH_3 + H, \tag{2a}$$

$$CH_3NH_3^+ + e \rightarrow CH_3 + NH_3. \tag{2b}$$

The exothermicity of the reactions is 358 (363), 51 (77), 405 (424) kJ mol^{-1} for Eqs. 2, 2a, and 2b, respectively (MP2/6-31G* and MP4/6-311G(d, p) in parentheses). Thus, once the ion $CH_3NH_3^+$ is formed, the dissociative recombination Eq. 2 proceeds with some probability.

Because $CH_3NH_3^+$ is isovalent with ethane CH_3CH_3, the ion is expected to be very stable. The exothermicity of the reaction Eq. 1 is certainly large, 497 (499) kJ mol^{-1}. This much energy must be released by the radiation in the radiative association reaction. If the electronic excited states of $CH_3NH_3^+$ is produced, the radiative association may proceed. But, the reaction potential energy surface between the ground states of methyl cation CH_3^+ and ammonia NH_3 is directly connected to the ground state of $CH_3NH_3^+$. Without any calculations, we can easily expect this characteristics of the reaction surface; a planer CH_3^+ has a vacant π orbital, and the nonbonding lone pair orbital of NH_3 forms a σ bond to the π orbital of CH_3^+. We examined the potential energy surface of the forming reaction to $CH_3NH_3^+$, and found that the ground state surface is smoothly connected to the product, as shown in the left side of Fig. 1. Thus, the radiative association through the electronic transition is not possible. The possible radiative process is the infra-red emission of the vibrationally hot ion $CH_3NH_3^+$. Now, we have to examine the possibility of producing the vibrationally hot ion.

In the previous paper[16] we systematically studied the reactions of hydrocarbon ions with hydrogen molecules, such as

$$CH_2^+ + H_2 \rightarrow CH_3^+ + H, \tag{5}$$

$$C_2H^+ + H_2 \rightarrow C_2H_2^+ + H. \tag{6}$$

These reactions are assumed to be followed by the dissociative recombination to form neutral hydrocarbons. The reactions are the key processes in forming larger carbon chains in the interstellar space. The characteristics of the potential energy surface of the reactions is that the reaction first proceeds to a stable intermediate (CH_4^+ in Eq. 5 and $C_2H_3^+$ in Eq. 6), and then, because the exothermicity of the reaction is large enough to break a C–H bond, the reaction proceeds further as in Eqs. 5 and 6. The reactions Eqs. 5 and 6 are apparently the hydrogen abstraction reactions, but they proceed only through the intermediate ions. A similar situation has to be examined in reaction Eq. 1; in other words, the ion $CH_3NH_3^+$ may be an intermediate to the reaction to $CH_3NH_2^+$+H. The right part of the curves in Fig. 2 is the schematic curve of the reaction. Because the left part of the reaction is the reaction between the closed shell systems, the single determinant wavefunction can approximately describe the forming reaction. On the other hand, the N–H breaking reaction forms a pair of the doublet states, and therefore, the single determinant description is expected to fail at larger N–H distances. The upper curve determined with the MP2 method has a barrier before the dissociation; the height is higher than the reactant CH_3^+ and NH_3. But the barrier disappears when the GVB(7) wave function is used; In the GVB(7) function, seven pairs of bonding and antibonding orbitals are coupled. The overall exothermicity of $CH_3^+ + NH_3 \rightarrow CH_3NH_2^+ + H$ is 26 with the MP2 method and 53 kJ mol^{-1} with the GVB method. Thus, similarly to the above reactions in hydrocarbon ions, the reaction proceeds to form a methylamine ion, unless the

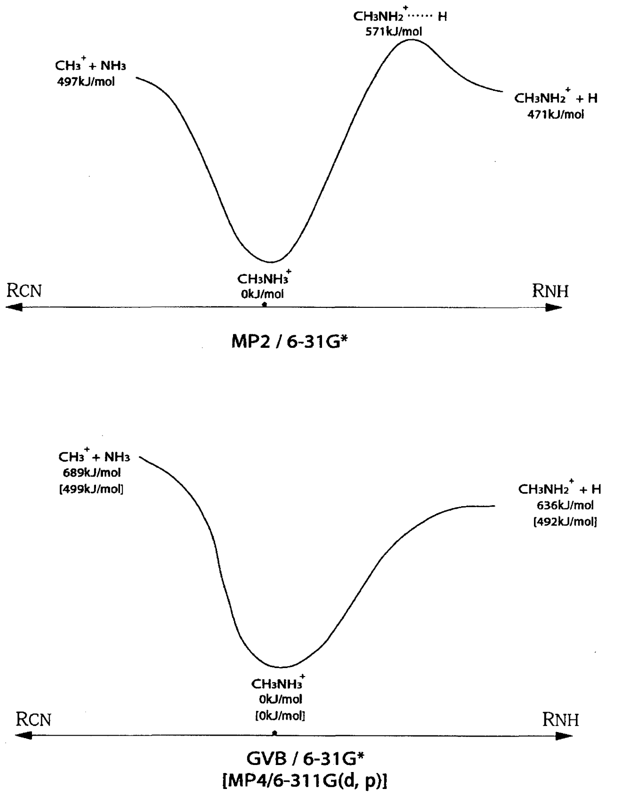


Fig. 2. The potential energy curves for reaction Eq. 1 with the MP2 and GVB approximations. The abscissa for the left part is the distance R_{CN} between C and N in arbitrary unit, and the one for the right part is the distance R_{NH} between N and the hydrogen which dissociates. At each R_{CN} and R_{NH} all the other geometrical parameters are optimized.

reaction energy is released by collisions with a third body or by a fast radiative decay at the intermediate complex ion. Nobes and Radom examined the condensation reaction of CH_3^+ with NH_3 to produce $CH_2NH_2^+$ and H_2.[17] Because their reaction path has a barrier, it is considered that the reaction to produce $CH_3NH_2^+$ and H is more advantageous than theirs.

Therefore, we have to look for an alternative mechanism for the formation of $CH_3NH_3^+$. One of the possible reactions is the reaction similar to Eqs. 5 and 6; the apparent abstraction reaction of an H atom from hydrogen molecule:

$$CH_3NH_2^+ + H_2 \rightarrow CH_3NH_3^+ + H. \qquad (7)$$

We examined the reaction path of this reaction Eq. 7 using the CASSCF (7, 7) method; In the CASSCF (7, 7), seven electrons and seven orbitals are included. We confirmed that there is no barrier in this reaction surface. The relative energy is shown in Fig. 3. In this case, the stable intermediate complex $CH_3NH_4^+$ is not found, as simply expected from the saturation of the valency of the nitrogen atom. Thus, by releasing a large exothermicity to the kinetic energy of a hydrogen atom, the ion $CH_3NH_3^+$ is formed, and then followed by the dissociative recombination Eq. 2; eventually neutral methylamine CH_3NH_2 is formed. If this new hypothesis were true, methylamine cation could be found in the interstellar space.

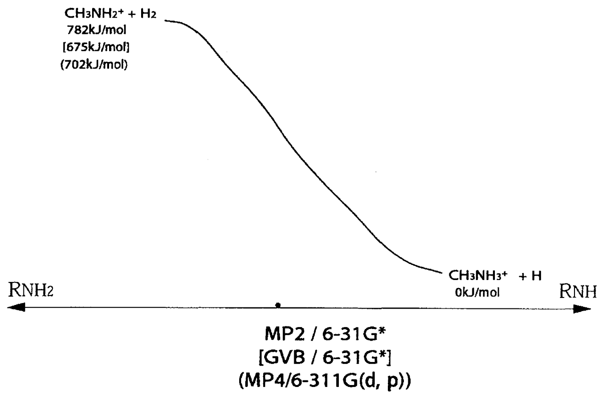


Fig. 3. The potential energy curves for reaction Eq. 6 with the MP2 [GVB] approximation. The abscissa for the left part is the distance R_{NH_2} between N and H_2 in arbitrary unit, and the one for the right part is the distance R_{NH} between N and the hydrogen which dissociates. At each R_{NH_2} and R_{NH} all the other geometrical parameters are optimized.

Methanol CH_3OH. The geometric structures and the relative energy of the reactant CH_3^+ and H_2O, the intermediate $CH_3OH_2^+$ and the product CH_3OH are shown in Figs. 4 and 5. They are in good agreement with the published data,[9,11,17,19—21] and some are slightly longer by 0.03 Å. Similarly to CH_3^++NH_3, a large exothermicity to form the intermediate is found. But, unlike CH_3^++NH_3, the reaction to produce methanol ion CH_3OH^+ is endothermic by 174 with the MP2 method and 145 $kJ\,mol^{-1}$ with the GVB(2) wave function; In the GVB(2) function, two pairs of bonding and antibonding orbitals are coupled. The collision of CH_3^+ and H_2O under low temperature cannot go to the right end of Fig. 5, but the system returns to the reactant or is trapped at the intermediate complex with very high internal energy. Since the reaction proceeds on a single potential energy surface, the excess energy at the intermediate complex is stored in the nuclear kinetic energy; translational, vibrational, and rotational. If the energy transfer from the translational motion to the vibrational and rotational motion, very hot intermediate molecular ions are produced, and the vibrational radiative association takes place to form $CH_3OH_2^+$ as reaction Eq. 3. Thus, Herbst's hypothesis holds for this reaction. It has been experimentally and theoretically revealed that the reaction of CH_3^+ with H_2O to produce CH_2OH^+ and H_2 does not proceed.[17]

Once the ion $CH_3OH_2^+$ is formed, the dissociative recombination proceeds. In this case, there are three possibilities of reactions: Eqs. 4, 4a, and 4b.

$$CH_3OH_2^+ + e \rightarrow CH_3OH + H, \qquad (4)$$

$$CH_3OH_2^+ + e \rightarrow CH_2OH_2 + H, \qquad (4a)$$

$$CH_3OH_2^+ + e \rightarrow CH_3 + H_2O. \qquad (4b)$$

The exothermicity of the reactions is 521 (505), 25 (47), 576 (605) $kJ\,mol^{-1}$ for Eqs. 4, 4a, and 4b, respectively (MP2/6-31G* and MP4/6-311G(d, p) in parentheses). Once the ion $CH_3OH_2^+$ is formed, the dissociative recombination Eq.

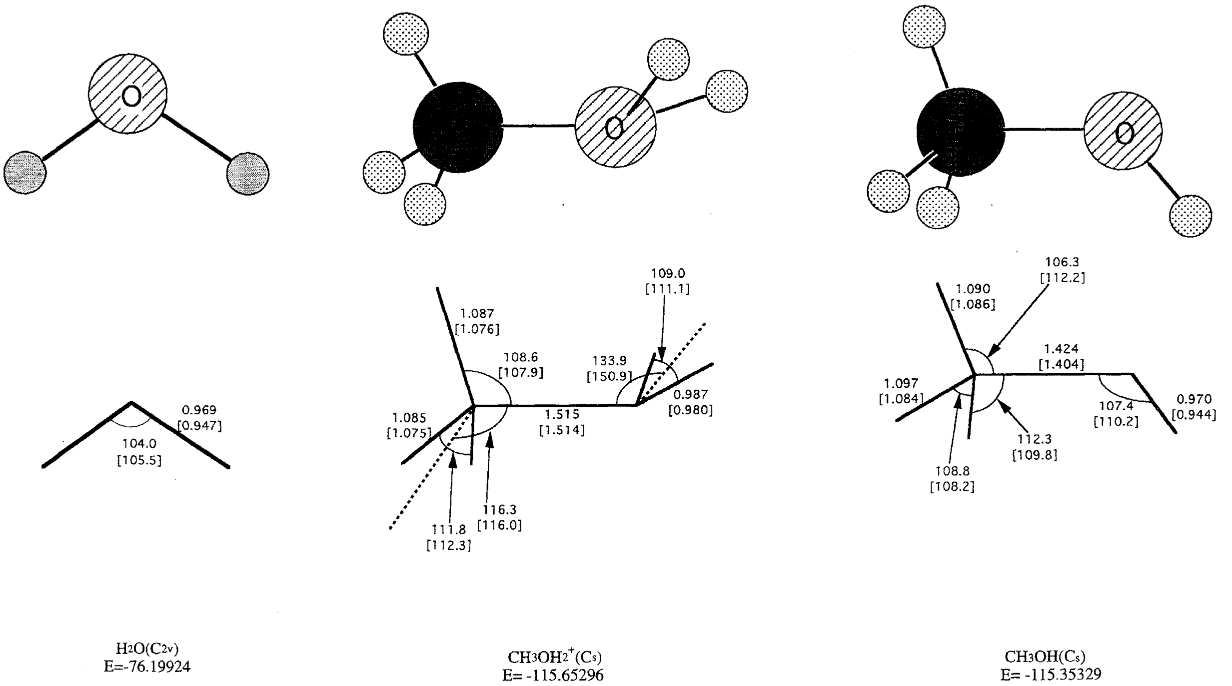


Fig. 4. Optimized geometries and total energies of the reactants and products of the reactions Eqs. 3 and 4 in MP2 level. Bond lengths in angstroms, angles in degrees, and energies in hartree.

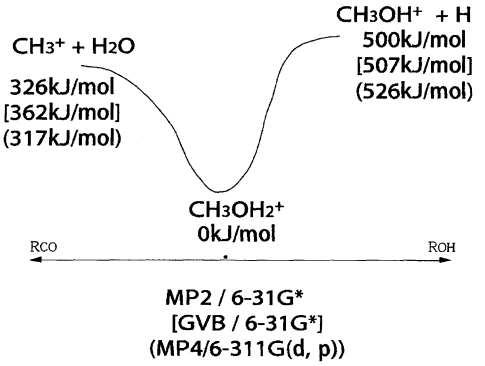


Fig. 5. The potential energy curves for reaction Eq. 3 with the MP2 [GVB] approximation. The abscissa for the left part is the distance R_{CO} between C and O in arbitrary unit, and the one for the right part is the distance R_{OH} between O and the hydrogen which dissociates. At each R_{CO} and R_{OH} all the other geometrical parameters are optimized.

4 proceeds with some probability, and eventually neutral methanol CH_3OH is formed.

Conclusion

1) Methylamine CH_3NH_2 cannot be formed via the two-step mechanism of Herbst's hypothesis.

2) We propose an alternative reaction mechanism forming CH_3NH_2:

$$CH_3^+ + NH_3 \rightarrow CH_3NH_2^+ + H$$
$$CH_3NH_2^+ + H_2 \rightarrow CH_3NH_3^+ + H$$
$$CH_3NH_3^+ + e \rightarrow CH_3NH_2 + H.$$

3) Methanol CH_3OH can be formed via the two-step mechanism of Herbst's hypothesis:

$$CH_3^+ + H_2O \rightarrow CH_3OH_2^+$$
$$CH_3OH_2^+ + e \rightarrow CH_3OH + H.$$

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