Committee VI
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Discussion Paper

by

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on

Ralph J. Cicerone's

METHANE IN THE ATMOSPHERE

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Comment on methane in atmosphere

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Methane CH_4 is one of a number of gases which has a green house effect to the earth environment. It absorbs i.r. region wave and intercepts terrestrial radiation. And the amount of mathane in atmosphere is now serious problem to consider future climatic change as well as the case of carbon dioxide on the earth. I would like to make some comments on methane in atmosphere.

1. Infra red absorption by some gases which have a green house effect.
2. How can we estimate excess methane in atmosphere ?
3. The effect of methane is equal to the effect of carbon dioxide converted from methane.
4. An evidence of existence of non biogenic methane in natural gas.

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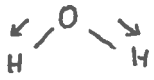
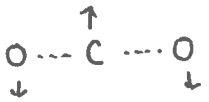
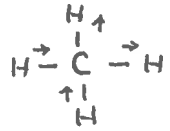
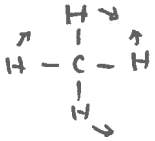
1. Infra red absorption by some gases which have a green house effect.

Typical vibration modes and infra red absorptions by some gases in atmosphere are shown in Fig. 1, in wave number cm^{-1}.

Fig. 1 molecular vibration and i.r. absorption

water			
H_2O	asym. stretching		3756
	sym. stretching		3657
	bending		1595
carbon dioxide			
CO_2	asym. stretching		2349
	bending		667
methane			
CH_4	asym. stretching		3019
	bending		1306

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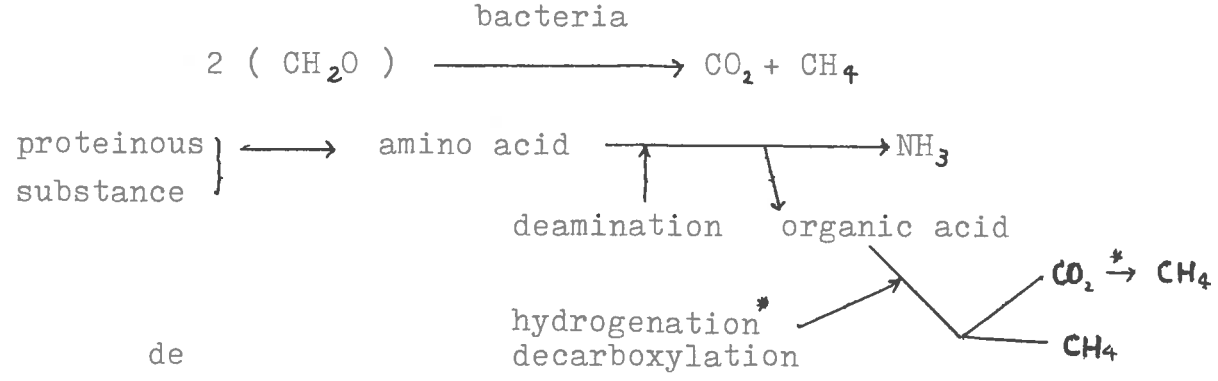
Ir. absorption of carbon dioxide 667 cm^{-1} corresponds to wave number to wave length of 15 μm.(0.8 μm= 12500 cm^{-1}, 4 μm = 2500 cm^{-1}). As shown above, ir absorptions by methane are 3019 cm^{-1} and 1306 cm^{-1} . These absorption are larger in wave number than that of carbon dioxide. The interception of terrestrial radiation by methane is smaller than that of carbon dioxide. It means that the green house effect by methane molecule itself does not so serious(?). The real effect will be discussed in section 3.

2. How can we estimate excess methane in atmosphere?

Is it really that content of methane in atmosphere is increasing ?

It is said that methane is produced naturally in large quantities from decay of organic matter. Methane is produced from anaerobic degradation of organic material. Typical cases are shown in Fig. 2.

Fig.2 Formation of methane from organic material



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It has been estimated in United States, that an average acre of swamp generates about 3000 pound of methane a year.

Naturally produced methane is balanced in nature as well as in the case of carbon dioxide cycle in nature. These natural processes may be balanced for long period from olden times, so the problem is how we can estimate excess methane which does not come from abiogenic sources.

Recently, fossil fuel such as petroleum, and natural gas have used by human being. More than 60 hydrocarbons have been identified in atmosphere. The major component is methane which is 90 % of total alkanes. This methane comes from decomposition of higher hydrocarbons. So the petroleum used by human being is one of major source of excess methane. Natural gas is used in world wide areas, because of high energy(high calorie), and clean energy compared with coal or sulfur rich oil. And main component of natural gas is methane. Natural gas is also one of the source of excess methane.

3. The effect of methane is equal to the effect of carbon dioxde converted from methane.

It is said that the principal natural source of carbon monoxide results from the oxidation of methane. And it is known that the process of nature which converts methane into carbon monoxide in turn converts the carbon monoxide into carbon dioxide. Also microorganisms in the soil affect the

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~~the~~ removal of carbon monoxide by oxidizing it to carbon dioxide.

These reaction will be understood with the bonding energy of these chemical species. Bonding energy concerned with some chemical bonds are shown in Table 1.

Table 1 bonding energy of some chemical bond

C -H	99 kcal/mol
C -O	84
C -C	83
C -Cl	78.5
C -F	105.4
H -H	104.2

As seen in Table 1, chemical bonding energy between carbon atom and hydrogen atom is 99 kcal/mol. This is smaller than C-F bonding energy. As known well, fluorocarbon such as tri-chloro fluoro methane $CFCl_3$ or dichloro difluoro methane CF_2Cl_2 is too stable to decompose in troposphere because of high stability of bonding.

As stated above, methane is easily oxidized in Troposphere, resulting carbon dioxide. So excess methane in atmosphere leads to the increase of carbon dioxide. Thus the effect of methane is equal to the effect of carbondioxde.

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4. An evidence of existence of non biogenic methane in natural gas.

Non biogenic methane in natural gas is reported by H. Wakita in the meeting of geochemical Society in Japan this autum.

In general, $^{3}He/^{4}He$ value of helium in natural gas is $(0.1\text{-}0.3)\times 10^{-6}$ and $\delta^{13}C$ of acompanying methane is -50~ -60 ‰. But natural gas from volcanic rock or green tuff area, contains He having high value of $^{3}He/^{4}He$ 9×10^{-6}, and $\delta^{13}C$ of methane is -40 ‰. Methane having high $\delta^{13}C$ was collected from east pacific ridge such as -20 ‰ or so. And the methane in volcanic rock or green tuff area is thought to be no biogenic.

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