FORMATION OF NOCTILUCENT CLOUD PARTICLES AND THE TEMPERATURE DISTRIBUTION AT THE POLAR MESOPAUSE

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Abstract: The relationship between the atmospheric condition of the polar mesosphere and the formation process of noctilucent cloud particles are discussed. The result suggests that the very low temperature found frequently in the summer polar mesosphere not only enables the noctilucent cloud particles to grow by water vapor condensation but also the nucleus to form through the ion-induced nucleation.

1. Introduction

During the summer above the polar region, at a height of 80 to 85 km, noctilucent clouds develop. Ground-based observations of noctilucent clouds have enabled us to estimate the size and number density of particles. Polarization measurements indicate that the radius of the particles is about 1 to 2×10^{-5} cm if we assume that particles have a monodisperse size distribution (WITT, 1960), while spectral intensity observations have shown that their concentration is in an order of 1 cm^{-3} (FOGLE and REES, 1972). Satellite observations show brightness due to the existence of particulate matter at the polar mesosphere and suggest a concentration of 15 particles cm^{-3} if the layer were assumed to be of 5 km thickness and to consist of uniform spherical particles with a radius of 1300Å (DONAHUE *et al.*, 1972).

Recently some investigators pointed out that the effect of the noctilucent cloud on the climatic change or on the ion balance of the ionospheric *D* region may not be negligible (HUMMEL and OLIVERO, 1976; HUMMEL, 1977; IWASAKA and THOMAS, 1979), so that it should be an interesting problem to clarify the nature of noctilucent cloud for application to the study of solar and mesospheric radiation, and ion chemistry in the polar mesosphere. Most previous researches have described the temperature dependence of the growing process of noctilucent cloud particles through the condensation of water vapor on ice crystals, but not the formation mechanism of these particles (nucleation process) (*e.g.*, CHRISTE, 1969; HESSTVEDT, 1962; REID, 1975; WITT, 1969). Although some investigators speculated that there was the possibility that various ions produced near the mesopause act as nuclei (*e.g.*, REID, 1975; ARNORD and JOOS, 1979), the detailed discussions have yet not been published.

In this paper, we should like to discuss the ion-induced nucleation process under the summer polar mesospheric conditions with respect to temperature distribution,

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ion density, and water vapor content.

2. Atmospheric Condition of the Summer Polar Mesosphere

Many investigators have shown that the temperature of the polar mesopause becomes very low; 160 K on the average and 140 K occasionally in summer season (*e.g.*, KOSHELOKOV, 1980; LABITZKE and BARNETT, 1979), and noctilucent clouds frequently develop in this region. The particles are formed by water vapor deposition onto the surface of condensation nuclei which, according to hypothesis, are provided by ion-molecular reactions.

According to the Clausius-Claypeyron equation, saturation vapor pressure is expressed by the following equation:

$$P_i = P_{i0} \exp\left[L_v m_w (1/T_0 - 1/T)/k\right], \quad (1)$$

where

P_i : the saturation vapor pressure,
P_{i0} : the known saturation vapor pressure at temperature T_0,
L_v : the latent heat of vaporization,
k : Boltzmann constant,
m_w : the mass of the water vapor molecule.

We shall assume that the particles are composed of ice; in this case the frost point temperature at which saturation occurs for a given vapor pressure P_s is given by:

$$T_f = T_0/[1 - (kT_0/(L_v m_w)) \ln (P_s/P_{i0})], \quad (2)$$

where

T_f: the frost point temperature.

In Fig. 1, the vertical profiles of the frost point temperature for various values of water vapor content (mixing ratio) are compared with the actual temperature profiles measured during the noctilucent cloud display. Obviously, supersaturation can occur with reasonable values of water vapor concentration over the region with a few kilometers width near the mesopause.

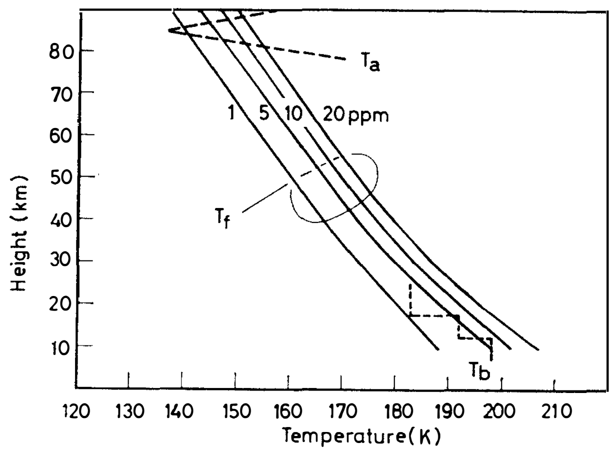

Fig. 1. Atmospheric temperatures, T_a and T_b, and frost point temperature, T_f. T_a is the measurement during noctilucent clouds display. Frost point temperatures, T_f are indicated for the water vapor mixing ratios of 1, 5, 10, and 20 ppmV.

3. The Ion-induced Nucleation in the Summer Polar Mesopause

Although the occurrence of supersaturation is a necessary condition for the growth of ice particles, it is not a sufficient condition. The spontaneous growth of particles in the absence of any condensation or sublimation nuclei is known as homogeneous nucleation, and in general requires high degree of super saturation, since the very small initial agglomerations of water vapor molecules tend to be broken up by thermal collisions with other molecules. The nucleation process is, however, greatly accelerated by the presence of small particles on whose surfaces the water vapor molecules can be collected in a protected environment. Suitable condensation nuclei are always present in the lower atmosphere, but their presence at the mesopause altitude is open to question. One way out of this difficulty invokes ions as condensation or sublimation nuclei.

Mass spectrometer observation (*e.g.*, ARNORD *et al.*, 1971; NARCISI *et al.*, 1972; GOLDBERG and AIKIN, 1971; JOHANNESSEN and KRANKOWSKY, 1972; MEISTER *et al.*, 1978; ZBINDEN *et al.*, 1975) have shown that the ionospheric D region is characterized by many positive and negative ions which result from external ionization processes leading initially to electron, molecular oxygen, nitrogen, and nitric oxide positive ions.

The homogeneous nucleation onto ions is discussed by STAUFFER *et al.* (1972), CASTLEMAN *et al.* (1978), CHAN and MOHNEN (1980), and others. Essentially the effect of the ion is to cause a decrease of the barrier of the Gibbs free energy required to form an "embryo" so that small cluster molecules formed around ions can grow into large particles if the condition is suitable.

The nucleation rate for this process is given by:

$$J=4\pi R^{*2}NN_i(kT/(2\pi m_a))^{1/2}\exp(-\Delta G^*/kT)\,, \tag{3}$$

where

N : the number density of water vapor molecule,
N_i : the number density of ion,
m_a : the mass of water vapor molecule,
T : the atmospheric temperature,

and R^* and ΔG^* are the "critical" radius and the Gibbs free energy change as defined below.

The classical Thomson equation states that the change in the Gibbs free energy required to form an "embryo" with an ion core of radius R_0,

$$\Delta G=-nkT\ln(p/p_\infty)+4\pi R^2\sigma+q^2(1-1/\varepsilon)(1/R-1/R_0)/2\,, \tag{4}$$

where

n : the number of water vapor molecule in a droplet,
p : the vapor pressure of water vapor,
p_∞ : the equilibrium vapor pressure,
σ : the surface tension,
ε : the dielectric constant of water vapor molecule,
R_0 : the radius of stable ionic molecular cluster.

The first term in eq. (4) will vary as R^3, so for very small values of R, ΔG will be dominated by the positive $4\pi R^2\sigma$ term or the third term showing the effect of the ion. Consequently, the formation of very small clusters of molecules requires an increase in the Gibbs free energy and is, therefore, strongly limited. On the other hand, ΔG is negative for large values of R for the case of $p/p_\infty > 1$, and the formation of large droplets is energetically favored. However, these droplets cannot be formed unless the molecular cluster grows large enough to overcome the Gibbs free energy barrier, due to the surface energy term. This energy barrier height is denoted by ΔG^*, and the radius for ΔG^* takes the "critical" value of R^*. Apparently the third term shows the lowering of the free energy due to the presence of the ion. In addition to this, we should like to point out that the lowering of the energy barrier is caused also by the large value of p/p_∞ in the atmospheric condition of the summer polar mesopause.

If $S = p/p_\infty$, there is supersaturation. Figure 2 shows schematically the variation of ΔG as a function of R with S as a parameter. One sees that when S becomes greater than unity $\mathrm{d}\Delta G/\mathrm{d}R = 0$ for $R = R_1$ and R_2. There is stable equilibrium at R_1 and unstable at R_2. As a particle whose radius is greater than R_2 grows continuously,

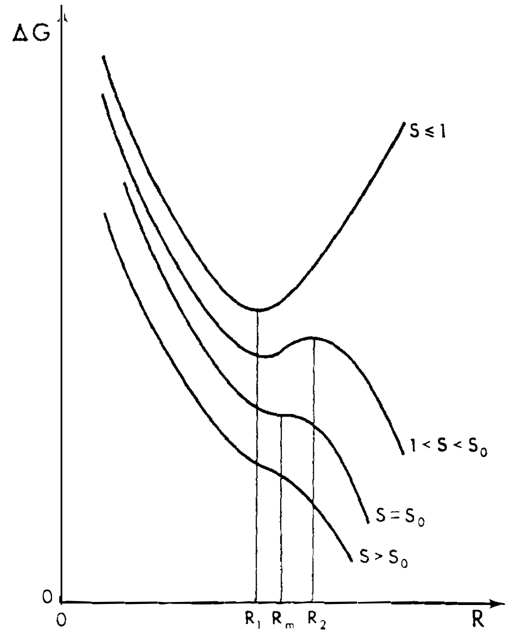

Fig. 2. Theoretical curves for the Gibbs free energy change ΔG as a function of particle radius R for different values of super-saturation ratio S. R_1 shows the stable radius of an ion cluster, R_2 is a limiting unstable radius. R_m represents the point of inflection for the condition of $S = S_0$. For $S > S_0$, particles will continue to grow. If $S < 1$, there are only stable states.

ΔG decreases in the range that R increases. The value of $R = R_m$ for $S = S_0$ is a special value corresponding to the point of inflection such as

$$R_m^3 = q^2 (1 - 1/\varepsilon)/(4\pi\sigma) \tag{5}$$

for $S > S_0$ there is always a growth of particles. For $S < 1$ there is only a stable state.

It is possible to present S as a function of R when there is equilibrium, *e.g.*, when $\mathrm{d}\Delta G/\mathrm{d}R = 0$. The curve shown in Fig. 3 is then obtained. This curve passes through a maximum at the value R_m. The portion of the curve for $R < R_m$ corresponds to states of stable equilibrium, where the part for $R > R_m$ represents unstable states. The radius R of a particle subjected to a vapor pressure represented by S increases if the point (S, R) applying to it is above the curve and decreases if the point (S, R) is suitably

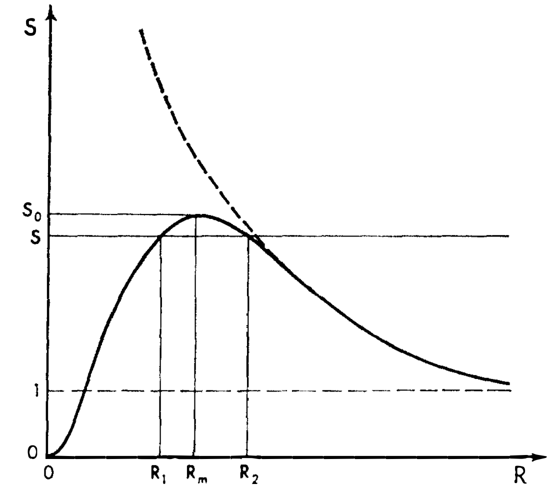

Fig. 3. *The function $S(R)$ of ionic particles for the condition of $d\Delta G/dR=0$. The values of R_1, R and R_2 are indicated. The dashed curve corresponds to $d\Delta G/dR$ for neutral particles. Here the particles are always unstable.*

below. The curve for $\mathrm{d}\Delta G/\mathrm{d}R=0$ for neutral particles is shown as a dotted curve.

In Fig. 4, we show the change of each term in eq. (4) under the reasonable condition of the summer polar mesopause: $T=140$ K, and water vapor mixing ratio$=1$ ppmV and 10 ppmV. Figure 4 suggests that $\mathrm{d}\Delta G/\mathrm{d}R<0$ is satisfied for any value of R under the atmospheric condition of $T=140$K, and water vapor mixing ratio$=10$ ppmV, and any ion cluster can grow to a large particle (noctilucent cloud particle).

Recently, very interesting results shown by CHAN and MOHNEN (1980) indicate that the saturation ratio, S at which the energy barrier vanishes and condensation

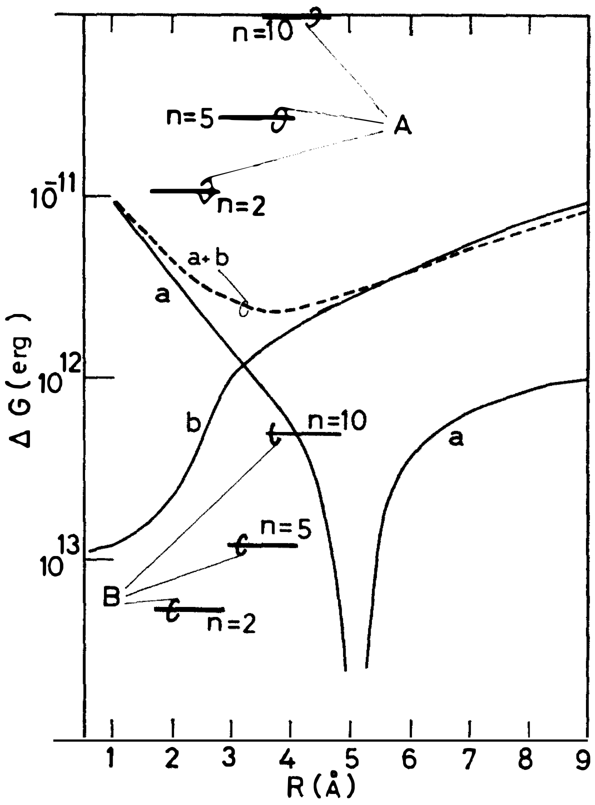

Fig. 4. *The variation of each term in the Gibbs free energy change equation for ionic particles (see text).*
a. The term showing the effect of ion (the right branch of curve "a" is for a negative value),
b. The term of surface tension effect.
The values of "$nkT \ln(p/p_\infty)$" are plotted for n in a reasonable range of n values. The values in A are represent the condition of $T=140$ K, and water vapor mixing ratio$=10$ ppmV, and values in B represent the condition, $T=140$ K, and water vapor mixing ratio$=1$ ppmV. Apparently, "$nkT \ln(p/p_\infty)$" term is larger than the curve, $a+b$, and ΔG becomes smaller with an increase of n for the atmospheric condition, $T=140$ K and water vapor mixing ratio$=10$ ppmV.

occurs on ions is 4.7 for a positive ion and 4.1 for a negative ion using the semi-molecular theory. The supersaturation ratio S is apparently smaller than the value $S \simeq 10$ for the atmospheric condition of $T=140$ K and water vapor mixing ratio$=10$ ppmV.

4. Conclusions and Discussion

In summary, the present study leads us to the following conclusions:

1) Assuming the constant mixing ratio of water vapor content is between 1 ppmV and 10 ppmV, supersaturation appears at the polar mesopause in summer season,

2) The high supersaturation ratio, about 10, found for $T=140$ K and water vapor content$=10$ ppmV allows not only the growth of noctilucent cloud particles but also the formation of an embryo through ion-induced nucleation.

Apparently, a great deal of further work is needed, particularly on the simultaneous measurements of clustering ion density, water vapor content, and atmospheric temperature at the polar mesopause, and on the nucleation process and its possible relation to the formation of water cluster ions. The key area in which knowledge is lacking is the transition from small ion clusters of molecular dimensions to macroscopic particles containing thousands of molecules. A clear understanding of the dynamics of this transition region would shed a great deal of light on the entire problem of particle formation in the atmosphere.

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