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ON THE FORMATION OF POLAR MESOSPHERIC CLOUD AND ECHO LAYERS

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Abstract: In this paper we show an effort to simulate ice particle formation from proton hydrates ($H^+(H_2O)_n$; PH) in the mesosphere. Our scheme stresses that the recombination of PHs with electrons plays a significant role to remove stable nucleus from the ionic system into the background neutral. In our tentative model, at $T=120$ K, $[H_2O]=6$ ppmV and $[e^-]=10^3\,cm^{-3}$, sufficient amounts of stable nuclei to form a noctilucent cloud are supplied within a layer of about 1 km thickness at 90 km height. The Polar Mesospheric Summer Echo (PMSE) layer is considered to be located at the formation region of heavy PHs. Vertical profiles of the layers of heavy PHs, PMSE and Polar Mesospheric Cloud are discussed.

1. Introduction

The noctilucent cloud (NLC) is considered to be the low latitude edge of the polar mesospheric cloud (PMC) found by satellite observations (DONAHUE *et al.*, 1972). The following three candidates for a cloud particle nucleus $\sim$ 10Å in radius have been considered (KEESEE, 1989). 1) meteor dust or meteor smoke, 2) cluster of meteor ions, or 3) heavy proton hydrates (PHs) formed from the major primary of NO^+ and O_2^+. Among them, 3) is more stable than 2). We can consider that observations showing an existence of heavy PHs strongly suggest that a proton hydration is an effective mechanism for the cloud formation. If 3) is the case, the polar mesosphere is considered to be a wall-less laboratory to show the whole process of nucleating ice particles from gas molecule, displaying along a large vertical scale with a long time constant.

The multi-national observations held in 1979 have shown quite interesting features on the formation of NLC, summarized below. A rocket-borne photometer observed at the altitude of 83 km a cloud layer of $\sim$ 1 km thickness, which consists of ice particles $\sim$ 1000Å in radius with a concentration of 10 to 100 cm^{-3} (BJÖRN *et al.*, 1985). In this NLC period, PHs up to n (hydration order) $=20$ are found at 90 km with a spectrum peak of $n=16$ (BJÖRN and ARNOLD, 1981). Approximate conditions for the cloud formation are considered as below (VON ZAHN and MEYER, 1989).

$$T<130\text{K},\quad [M]\sim 1\times 10^{14}\,cm^{-3},\quad [H_2O]=1\sim 10\,\text{ppmV},\quad [e^-]\sim 10^3\,cm^{-3}$$
$$I\sim 10\,cm^{-3}\,s^{-1},\quad \eta\sim 10^{-11},$$

where I is the ionization rate and η is the ionization degree.

Ionic nucleation is quite rapid in comparison with a homogeneous case due to the reduction of the energy barrier by ionic force. At present, however, ion chemistry of heavy PHs remains as major problems in the mesospheric chemistry (REID, 1989). The whole process forming NLCs with ionic nucleation has not yet been treated, because the effect of the recombination with electrons complicates the phenomena (KEESEE, 1989). ARNOLD (1980) has stressed the role of recombination in the formation of heavy PHs at the mesospause. In this paper, we model the formation of PMC according to a simple ion nucleation scheme proposed by SUGIYAMA (1991). We also discuss the formation of the Polar Mesospheric Summer Echo layers recently found by VHF radars (ECKLUND and BALSLEY, 1981; JENSEN *et al.*, 1988) in relation to the formation of the cloud.

2. Scheme of Ionic Nucleation with Recombination

In the theory of nucleation, an unstable equilibrium inevitably occurs beyond the critical size n^*. If the macroscopic particles exist within the system, they rapidly consume the raw materials in the gas so as to change drastically the initial conditions of the nucleation (YAMAMOTO and HASEGAWA, 1977). A steady state nucleation system is maintained only if the nucleation flow J removes large size particles from the system (FEDLER *et al.*, 1966).

Because the recombination is an exothermic reaction, the stability of the cluster in recombination must be considered to depend on its size (ARNOLD, 1980). We define n_S so that an ion cluster with $n<n_S$ evaporates in the recombination, and a cluster with $n>n_S$ is stable (non-evaporate) due to the large degrees of freedom. Focusing on the effect of recombination, SUGIYAMA (1991) has proposed a simple picture of the steady nucleating system in that the nucleation rate J is essentially contributed by the recombination of $n>n_S$ clusters. Following SUGIYAMA (1991), we consider a nucleation in a system with very low ionization degrees.

$$\begin{array}{ccccccc} A_{n-1} & \underset{r_n}{\overset{f_{n-1}}{\rightleftarrows}} & A_n & \underset{r_{n+1}}{\overset{f_n}{\rightleftarrows}} & A_{n+1} \\ \downarrow & & \downarrow & & \downarrow \\ Rec_{n-1} & & Rec_n & & Rec_{n+1} \end{array} \qquad (1)$$

Here A_n is a cluster with n ligands, and f_n, r_n and Rec_n represent the frequencies of the forward reaction, backward reaction and recombination with electrons, respectively. The following Master equation governs the clustering.

$$\frac{d[n]}{dt} = f_{n-1}[n-1] - r_n[n] - \{f_n[n] - r_{n+1}[n+1]\} - Rec_n[n] - L_n[n] \qquad (2)$$

Hereafter $[n]$ represents the concentration of A_n. At the initial step, we must add the ionization rate I on the right hand side of (2). In (2), L_n represents the loss frequency due to the removal of macroscopic particle from the nucleation system by some process other than recombination. In our case, the descent of macroscopic

particles due to gravity is responsible for L_n, which is approximately described as follows.

$$L_n = \frac{v_n}{l} \tag{3}$$

where v_n is the downward velocity of the n-th cluster and l is the thickness of the nucleation layer. The main assumption in this paper is

$$L_n \ll Rec_n \tag{4}$$

for n-th cluster of which concentration is not negligible. As (4) is the case of our interest (see section 4) hereafter we set $L_n = 0$.

To obtain the size spectrum of the steady state system, (2) is solved with the boundary condition of $[n] = 0$ for $n = \infty$, which is brought about by the removal flow from the system getting rid of its instability. To maintain a steady state, one must anticipate the corresponding incoming flow with the removal one. Law material, H_2O in our case, is assumed to be steadily supplied from below by diffusion. The main concept of SUGIYAMA's scheme lies in the simple physical process in the steady ionic-nucleation system, that the removal flow is a part of the recombination flow and the incoming flow is the corresponding part of the ionization rate. On the one hand, the recombination flow, in general, consists of two components,

$$\begin{aligned}\text{Recombination flow} = &(\text{evaporation flow};\ n < n_S)\\ &+(\text{non-evaporate flow};\ n \geq n_S)\end{aligned} \tag{5}$$

On the other hand, the nucleation flow, in general, consists of two components,

$$J = (\text{Recombination flow at } n \geq n_S) + (\text{Descent flow due to gravity}) \tag{6}$$

In our case of $L_n = 0$, J is approximately given as

$$J \approx (\text{non-evaporate Recombination flow at } n \geq n_S) \tag{7}$$

We illustrate in Fig. 1 a scheme of the flows in the steady ionic system. The net forward flow at n: F_n, supplies such amount of clusters as are lost by recombination occurring beyond n.

$$F_n \equiv f_n[n] - r_{n+1}[n+1] \tag{8}$$

Then (7) gives the nucleation rate as

$$\begin{aligned}J = F_{n_S} &= \sum_{n_S}^{\infty} Rec_n[n]\\ &= f_{n_S}[n_S] - r_{n_S+1}[n_S+1]\end{aligned} \tag{9}$$

In an effective nucleating system, we consider that f_{n_S} is considerably greater than r_{n_S+1}, then (8) gives a simple, although rough, estimate of J as

$$J \approx f_{n_S}[n_S] \tag{10}$$

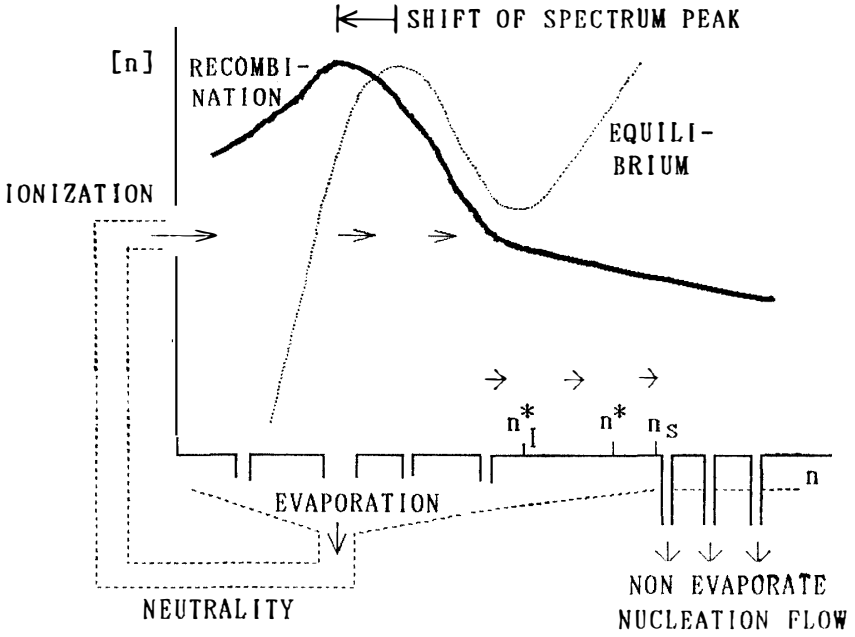

Fig. 1. A scheme of the ionic nucleation with recombination. n_1^*, n^* and n_S are the critical sizes of the ionic equilibrium system, that of the neutral system and the stable cluster in recombination, respectively. In this scheme the nucleation flow is contributed from the recombination occurring at $n>n_S$.

3. A Model of Proton Hydrations with Recombination

To obtain the spectrum of PHs, we need all coefficients of (2). The relations between the coefficients of the chemical reactions and the reaction frequencies are as follows.

$$f_n=k_{f,n}[\mathrm{M}][\mathrm{H_2O}],\quad r_n=k_{r,n}[\mathrm{M}],\quad Rec_n=\alpha_n[\mathrm{e^-}] \tag{11}$$

Laboratory data of the reaction coefficients of the proton hydrations for $n\leq 6$ are reported by LAU *et al.* (1982) and the recombinations for $n\leq 6$ by LEU *et al.* (1973). We will extrapolate reaction coefficients of the proton hydrations up to $n=200$ in the following procedure.

1. We evaluate the Gibbs free energy for the cluster formation by using the Thomson ionic nucleation theory described as below (KEESEE, 1989).

$$\Delta G_n=-nkT\ln S+n^{2/3}4\pi a_1^2\sigma_0-\frac{e^2}{2\varepsilon_0}\left(1-\frac{1}{\varepsilon}\right)\left(\frac{1}{a_1}-\frac{1}{n^{1/3}a_1}\right) \tag{12}$$

where S is the super saturation ratio and a_1 is the mean radius of an H_2O molecule in liquid. σ_0, ε_0 and ε are the surface tension of bulk water, the dielectric constant of vacuum and that of water, respectively.

2. The forward reaction coefficients $k_{f,n}$ are determined through the three-body reactions, *i.e.* combination, stabilization and decomposition. We extrapolate k_f with the simplified Kassel equation (LAU *et al.*, 1982), using additional enthalpy

to form n from $n-1$ th cluster, $\Delta H_{n-1,n}$, obtained from (12), and assumed degrees of freedom of a cluster. Although the evaluation itself might be quite ambiguous, at low temperatures for large clusters such as $n>10$, the decomposition is so slow that the reaction is governed merely by the composition. Then we give $k_f[M]=k_L$ (Langevin rate) $=1\times10^{-9}$cm^{-3}s^{-1}, which is used in the ion molecular reactions. Thus the ambiguity is essentially pushed aside for $n>10$, and for small n, we can fortunately refer to laboratory data. The coefficients of the backward reaction $k_{r,n}$ are obtained from (12) and $k_{f,n}$.

3. The coefficients of the recombination with electrons have been measured to be constant around $n=5$, rather than to increase monotonically with cluster size (HUANG *et al.*, 1978), then we set $\alpha_n=5\times10^{-6}$cm^{3}s^{-1}.

We illustrate (12) in Fig. 2 with $\sigma_0=80$ dyne/cm and $\varepsilon=80$ (the bulk value of liquid water). This figure shows that the free energy has its constant turning point of curvature at $n=31$ for various S. In Fig. 3 we show the derivative form of (12) with respect to n, that is $\Delta G_{n-1,n}$: additional free energy to form the n-th cluster from the $n-1$ th. Zero level in this figure corresponds to $S=1$, thus it is biased with the bulk latent heat H_0 which we take $H_0=10$ kcal/mol $=0.43$ eV/molecule in order to fit the experimental value of $n=8$ (KEBARLE *et al.*, 1967).

We show in Fig. 4 steady state spectra of PHs obtained with coefficients mentioned above, for various T, $[H_2O]$ and $[e^-]$. In the case of Fig. 4a, at which $T=120$ K, $[H_2O]=6$ ppmV and $[e^-]=10^3$cm^{-3}, the magnitudes of the reaction frequencies are as follows.

$$Rec_n=5\times10^{-3}\,s^{-1}\ll r_n<f_n\approx0.1\,s^{-1}$$

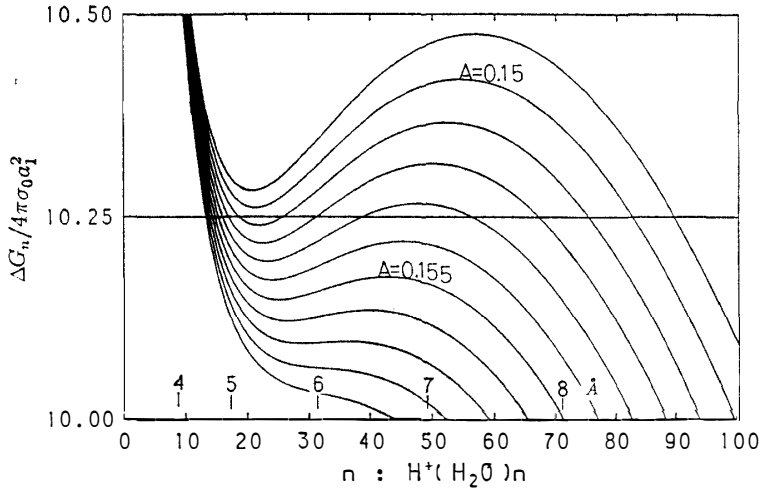

Fig. 2. Gibbs free energy of n-th PH given by (12), normalized by the surface free energy per a H_2O. $G_n/4\pi\sigma_0 a_1^2=-An+Bn^{2/3}+Cn^{1/3}$ with $B=1$, $C=16$ and various A. We apply $\sigma_0=80$ dyne/cm and $\varepsilon=80$ and $a_1=1.93$ Å. $A=0.15$ corresponds to $S=4.66$ at $T=264$ K or $S=29.5$ at $T=120$ K. $A=0.16$ corresponds to $S=5.16$ at $T=264$ K or $S=37$ at $T=120$ K. Values in Å are the radius of the cluster.

Figure 4 shows how the size spectrum of PHs depends on [e^-] as well as T and [H_2O].

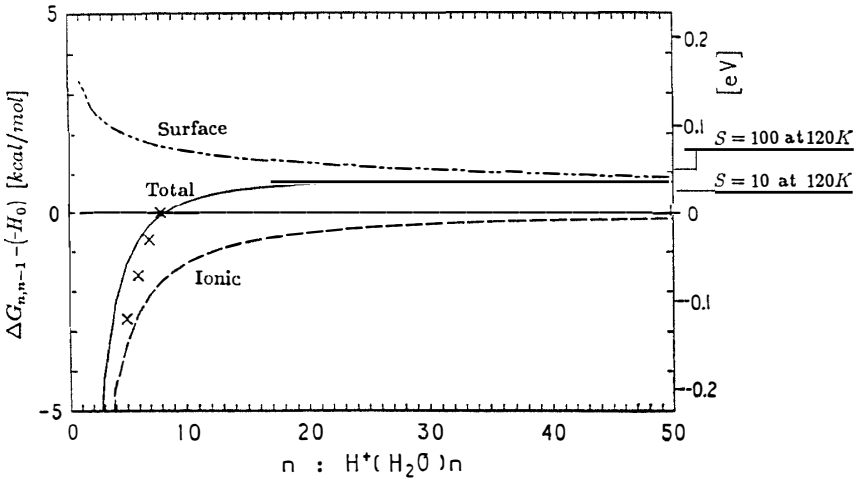

Fig. 3. Additional free energy calculated by (12) to form n-th PH from (n−1)-th. Chain, broken and bold lines represent surface, ionic and total energy, respectively. Cross marks are experimental values by LAU et al. (1982) and KEBARLE et al., (1967). H_0 is the bulk latent heat assumed as 10 kcal/mol to fit laboratory data of n=8.

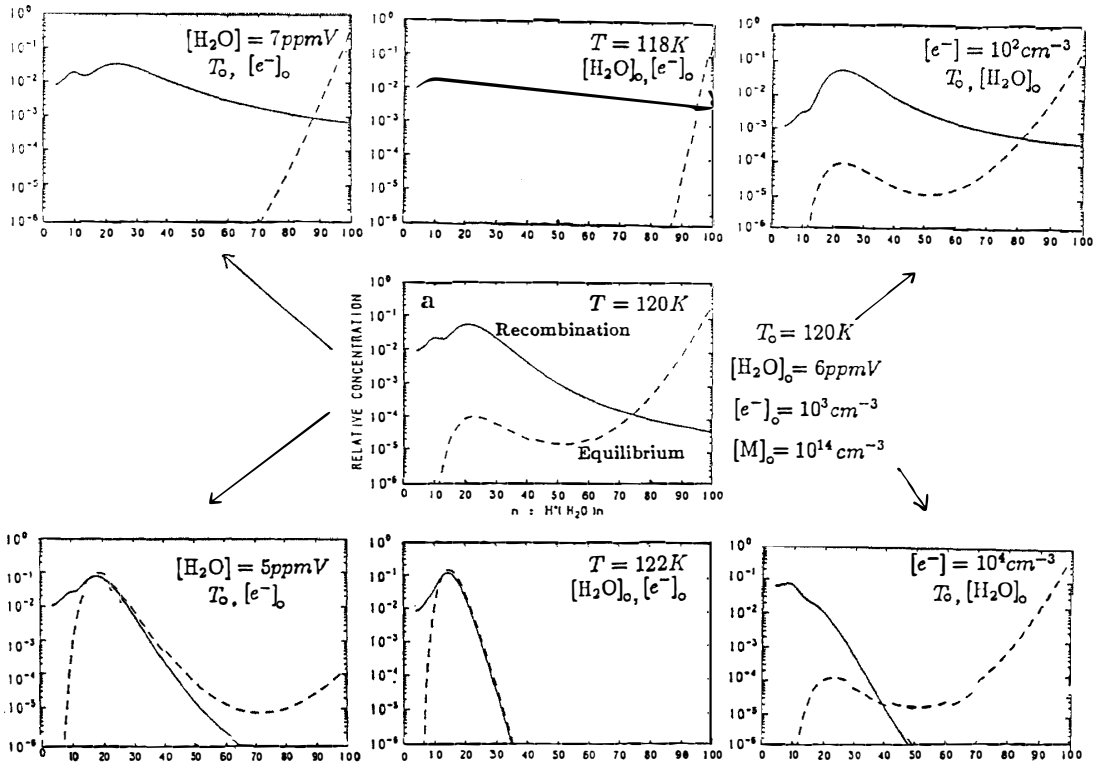

Fig. 4. Results of model spectra of PHs under various conditions. (a) is the case of T=120 K, [H_2O]=6 ppmV, [e^-]=10^3 cm^{-3} and [M]=10^{14} cm^{-3}. Others are spectrum variation from (a) due to the changes of [H_2O], temperatures and [e^-].

4. Nucleation and Growth of Ice Particles

We apply the nucleation scheme shown in section 2 to the clustering model in section 3. The problem is how to evaluate the critical size, n_S, which is stable against the recombination. On the one hand, the released energy in the recombination of H^+ and e^- corresponds to the total bond energy of the cluster with $n=13.6/0.43=31$ ligands. Further, we can speculate the case in which the positive and negative hydrates coexist within the cluster, because, the laboratory experiments show that $n=21$, $H_3^+O(H_2O)_{20}$, is quite stable owing to its symmetric structure (SHINOHARA, 1987) and the hydrated electrons in the liquid water is thought to consist of at most $n=10$ to 20 H_2O molecules. On the other hand, the growth of the recombined neutral cluster in the background neutral system takes place only when $n^*<n_S$. The critical size in neutral system, n^*, is estimated from (12) with $e=0$ as $n^*\approx 80$ for the conditions of Fig. 4a. The estimate of J may not depend strongly on the precise choice of n_S, because, as shown in Fig. 4a, the spectrum dependence on n is weak. Therefore we assume $n_S=80$ ($\sim$ 8Å in radius), then the nucleation rate is estimated from (10) as

$$J\approx 1\times 10^{-2}\text{cm}^{-3}\text{s}^{-1}$$

in the case of Fig. 4a where $T=120$ K, $[H_2O]=6$ ppmV, $[M]=10^{11}$ cm^{-3}, $[e^-]=10^3$ cm^{-3}, and where we get $[n_S]=0.1$ cm^{-3} and $f_{nS}=0.1$ s^{-1} at $n_S=80$. The ratio of obtained J to the ionization rate I is 1/1000.

We illustrate in Figs. 5 and 6 a conceptual picture of the formation of the polar mesospheric cloud based on the observations and the considerations above, with the help of the growth model given by REID (1975). The heavy PH formation layer at 90 km height is quite thin due to a strong variability of temperature and humidity, and part of this layer is the nucleation layer producing neutral particles with $n>n_S$ by recombination, which are accumulated just below the layer due to the gravitational effect. These neutral nuclei continue to fall about 7 km until they reach the size

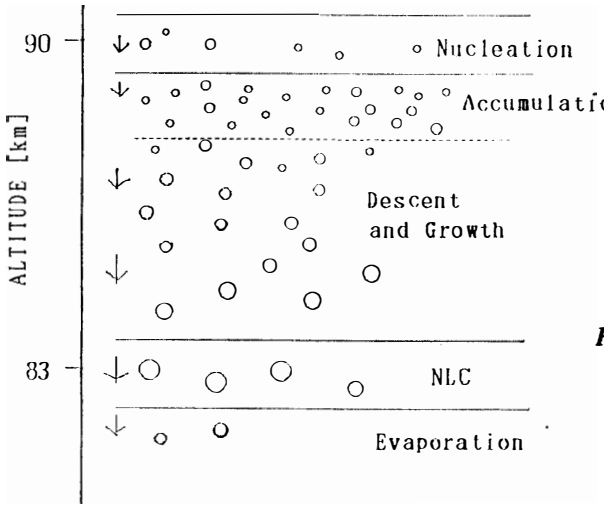

Fig. 5. A picture of the vertical distributions of ice particles formed through PHs.

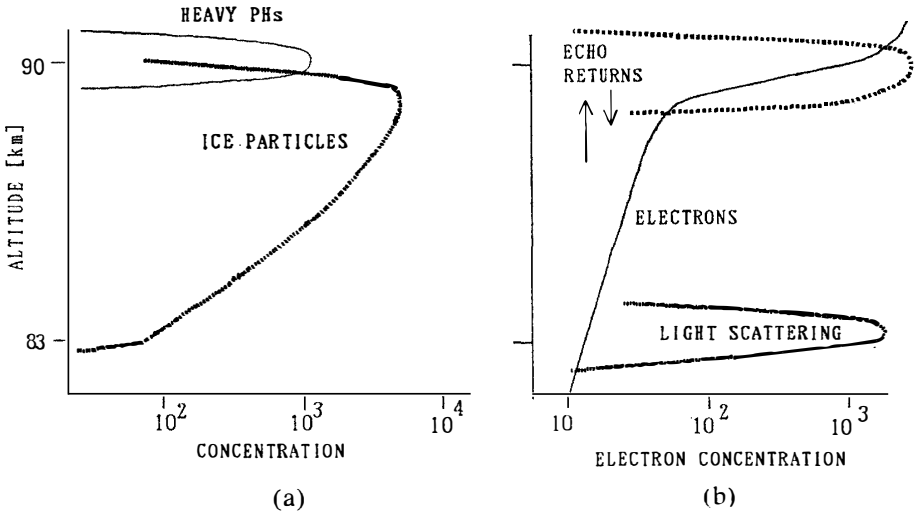

Fig. 6. A conceptual distributions of (a) concentration of heavy PHs and ice particles, and (b) electrons, echo returns and light scatterings.

optically visible. The descent velocity is proportional to the radius of the particles (REID, 1975), and we obtain $v \approx 1$ cm s^{-1} at $r = 8$Å and $v \approx 100$ cm s^{-1} at $r = 1000$Å. If we neglect, for simplicity, the aggregations of the particles, and if there is no evaporation in the growth region, then, with the use of the conservation of particle numbers: $v[n] = \text{constant}$, we conclude that the concentration of neutral particles in the accumulation region must be about 100 times that of the cloud region. Therefore, as illustrated in Fig. 6a, to supply the observed NLC particles of 10^{1} cm^{-3}, we anticipate that particles with $n \geq 80$ are accumulated as much as $\sum_{ns}^{\infty}[n]_{\text{neutral}} = 10^{3}$ cm^{-3} just below the nucleation layer. Then the required thickness of the nucleation layer is estimated as $l \approx 1$ km from the conservation of particle numbers at the accumulation region;

$$\sum_{n>ns}^{\infty} v_n[n]_{\text{neutral}} = Jl \tag{13}$$

with the approximation of $v_n \approx v_{ns}$. The ion loss rate due to gravity is estimated as

$$L_n = \frac{v_{ns}}{l} \approx 1 \times 10^{-5}\text{s}^{-1}, \tag{14}$$

therefore the assumption of (4) is valid. NLC is found at the bottom part of the ice particle profiles, for the cross section of Rayleigh scatterings depends on 6-th powers of the radius of small particles. At the base of the mesopause, particles may evaporate due to high temperatures.

5. Formation of Echo Layers

KELLEY *et al.* (1987) have discussed the cause of PMSE due to a reduction in the turbulent scale of electrons effected by heavy PHs. As shown in Fig. 6b, we speculate that there is a strong gradient of electron concentration at the heavy PH

layers due to large values of recombination coefficients of PHs (SUGIYAMA, 1988). We consider that this gradient must be another cause of the Polar Mesospheric Summer Echo, because a strong radar reflection in the mesosphere requires strong fluctuations in electron concentration which occur within the region of steep gradient of electron density with predominating small-scale turbulences (MURAOKA *et al.*, 1988, 1989). If the heavy PHs are formed at lower altitudes, then the particle growth may not attain visible size owing to the temperature structure of the mesopause. In this case a radar echo may occur but NLC does not. Correlations between altitude variations of PMSE layers and occurrence of NLC will give important tests whether NLC is formed through PHs or not.

6. Discussions

We have evaluated nucleus formation with the use of extrapolated values of the reaction coefficients which inevitably may have some ambiguities. In our numerical model, we obtain $T=120$ K for NLC condition, which may be too low in comparison with observations. This result is a tentative one obtained by fitting H_0 to the laboratory data of the clustering at $n=8$. This value of H_0 is about 10% smaller than the latent heat of the ice. If we set H_0 10% larger than we applied, then T appropriate for NLC condition becomes nearly 10% larger.

Further, we obtained a picture of the NLC formation with rather rough estimations. We have neglected such effects as the eddy diffusion of nuclei and aggregations. Accordingly, further studies to form NLC are necessary in many respects. We believe that the theories of such complicated phenomena as nucleation in plasma are improved through close comparison with observations, and we assert that the polar mesosphere is an irreplaceable well-less laboratory for this study.

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