

# Formation and implications of ice particle nucleation in the stratosphere

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**Abstract.** The classical nucleation theory of homogeneous freezing along with a thermodynamic model of aqueous  $\text{HNO}_3$  is used to calculate the critical temperatures and compositions at which ice crystals will nucleate from an aqueous  $\text{HNO}_3$  droplet. Assuming that stratospheric aerosols are composed of aqueous  $\text{HNO}_3$  near the ice frost point, we show that ice particle formation in the stratosphere can only occur if the air mass is cooled to about 2 to 3 K below the equilibrium condensation point of ice. A simple function is given for predicting the nucleation temperature of ice particle formation in the stratosphere from the ambient water vapor concentration. Microphysical calculations show that only fast cooling rates ( $> 500 \text{ K day}^{-1}$ ) encountered in cold lee waves are rapid enough for nucleating the majority of the background aerosols into ice particles. The likelihood that ice crystals formed in lee waves may result in the subsequent crystallization of  $\text{HNO}_3$  in the droplets is discussed. The barrier to ice formation by heterogeneous gas phase nucleation is compared to that of homogeneous freezing nucleation.

## Introduction

It was first suggested by Dye *et al.* [1992] that stratospheric sulfate aerosols can remain supercooled to very low temperatures. Prior to the work of Dye and co-workers it was assumed that stratospheric aerosols freeze at temperatures well above the equilibrium condensation point of Type I ( $\text{HNO}_3$ -containing aerosol) and Type II (ice clouds) polar stratospheric clouds (PSCs). Thus in previous PSC formation theories it was naturally assumed that the nucleation process would occur by deposition of  $\text{HNO}_3$  and  $\text{H}_2\text{O}$  vapors on the surfaces of frozen sulfate aerosols [e.g., Turco *et al.*, 1989; Toon *et al.*, 1989]. However the fact that sulfate aerosols can remain liquid to such low temperatures would imply that at least the initial cycles of PSC formation must occur in liquid solutions. Later laboratory and modeling studies showed that sulfate solutions can remain supercooled to very low temperatures and at the same time uptake  $\text{HNO}_3$  from the vapor phase to form a ternary solution droplet of  $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$  [Zhang *et al.*, 1993; Molina *et al.*, 1993; Tabazadeh *et al.*, 1994; Carslaw *et al.*, 1994]. These ternary droplets are now known as Type Ib PSCs. Currently thermodynamic equilibrium calculations are available for modeling the formation, growth and evaporation of Type Ib PSC under stratospheric conditions [Tabazadeh *et al.*, 1994; Carslaw *et al.*, 1994]. However, the mechanisms by which solid Type Ia or Type II PSCs can form in the stratosphere have remained somewhat elusive [Tolbert, 1994].

In recent years several studies have suggested various pathways for the formation of solid Type Ia PSCs, some of which suggest nucleation of Type Ia PSCs on the surfaces of Type II PSCs [e.g., Tolbert, 1994; Koop *et al.*, 1995]. Therefore in order to include such mechanisms in the microphysical modeling of Type I PSCs would first require predicting the occurrence of Type II PSCs. In this paper we outline an algorithm for the formation of Type II PSCs from homogeneous freezing of ice crystals from a nearly aqueous  $\text{HNO}_3$  solution droplet. Previous studies have shown that under winter polar stratospheric conditions ternary droplets become nearly aqueous  $\text{HNO}_3$  at temperatures close to the ice frost point [Tabazadeh *et al.*, 1994a; Carslaw *et al.*, 1994]. Thus we believe that modeling ice nucleation from an aqueous  $\text{HNO}_3$  solution droplet is a good analog for ice particle formation in the stratosphere.

## Data Parameterization

The results from the Clegg and Brimblecombe [1990] aqueous  $\text{HNO}_3$  thermodynamic model, which are based on many laboratory studies on the physical properties of aqueous  $\text{HNO}_3$ , are fitted into analytical functions (Table 1). These analytical functions express the variation in the aqueous  $\text{HNO}_3$  solution composition with temperature and water activity. We note that Clegg and Brimblecombe state that their model is valid in the temperature range of 213 to 393 K. However we have previously used the results of this model to calculate the composition of ternary aerosols in the stratosphere to very low temperatures ( $< 188 \text{ K}$ ) and have shown that the parameters described by this model extrapolate well to low temperatures [Tabazadeh *et al.*, 1994]. Thus we have confidence that the aqueous  $\text{HNO}_3$  model of Clegg and Brimblecombe extrapolates well to lower temperatures. The parameterization scheme used here to derive the functions given in Table 1 is identical to that described in our previous work on the aqueous  $\text{H}_2\text{SO}_4$  system [Tabazadeh *et al.*, 1997a]. Using the functions given in Table 1, the aqueous  $\text{HNO}_3$  composition can be calculated from

$$m_n(a_w, T) = y_1(a_w) + \frac{(T-190)[y_2(a_w) - y_1(a_w)]}{70} \quad (1)$$

Where  $m_n$  is the nitric acid molality, and  $a_w$  is the water activity. The  $y$  functions are given in Table 1. Note that the acid weight percent ( $w_n$ ) and molality are related by

$$w_n = \frac{6300m_n}{63m_n + 1000} \quad (2)$$

This parameterization is valid for all relative humidities in the temperature range of 180 to 230 K and differs from the results of the Clegg and Brimblecombe model by no more than 1 %.

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Paper number 97GL01883.  
0094-8534/97/97GL-01883\$05.00

**Table 1.** Composition Functions

| $y = Aa_w^B + Ca_w + D$ |                  |                  |                  |                  |
|-------------------------|------------------|------------------|------------------|------------------|
|                         | A                | B                | C                | D                |
| $a_w < 0.05$            |                  |                  |                  |                  |
| $y_1$                   | 5.6811966385e+0  | -5.2781515793e-1 | 1.7844655060e+2  | -1.9944014406e+0 |
| $y_2$                   | 9.0405763286e+0  | -5.4424836165e-1 | 5.3246079021e+1  | 4.6674594268e+1  |
| $0.05 < a_w < 0.6$      |                  |                  |                  |                  |
| $y_1$                   | 7.9415477295e+0  | -4.0853067200e-1 | -1.0675959795e+1 | 5.7733271636e+0  |
| $y_2$                   | 9.5033394917e+0  | -5.3655348172e-1 | -1.3366846037e+1 | 4.5796103358e+0  |
| $a_w > 0.6$             |                  |                  |                  |                  |
| $y_1$                   | -2.0846136893e+2 | -1.3840491342e-1 | -5.9746717399e+1 | 2.6848564500e+2  |
| $y_2$                   | -2.2406176695e+2 | -3.0723152773e-2 | -3.1163742477e+1 | 2.5542273520e+2  |

Read 5.6811966385e+0 as 5.6811966385 x 10<sup>0</sup>. The water activity ( $a_w$ ) is the ratio of the ambient water vapor concentration to the saturation water vapor pressure over liquid water. To be consistent with the composition calculations, the liquid saturation water vapor pressure (mb) should be evaluated from equation (1) in *Tabazadeh et al.* (1997a).

### Homogeneous Freezing Nucleation Theory

A detailed mathematical description for homogeneous freezing of ice from an aqueous solute solution droplet is described elsewhere [*Tabazadeh et al.*, 1997b]. Here we only show a few key equations. The rate of ice nucleation from an aqueous HNO<sub>3</sub> solution droplet in units of particle per second is given by

$$J = Ce^{-(\Delta F_g + \Delta F_{act})/kT} \quad (3)$$

where  $C$  (particle<sup>-1</sup> sec<sup>-1</sup>) is the preexponential factor,  $\Delta F_g$  (ergs) is the free energy for the formation of the ice germ,  $\Delta F_{act}$  (ergs) is the diffusion activation energy of water molecules across the ice/nitrate solution phase boundary,  $T$  (K) is temperature, and  $k$  is the Boltzmann constant.

Recently, we derived  $\Delta F_{act}$  values for the H<sub>2</sub>SO<sub>4</sub> system from recent laboratory experiments on ice nucleation from aqueous H<sub>2</sub>SO<sub>4</sub> solution droplets [*Tabazadeh et al.*, 1997b, *Bertram et al.*, 1996]. For the ice nucleation calculations given below we used the same diffusion activation energy ( $\Delta F_{act}$ ) that we derived for the H<sub>2</sub>SO<sub>4</sub> system. We note that for a given composition the viscosity of solution is higher for aqueous H<sub>2</sub>SO<sub>4</sub> as compared to aqueous HNO<sub>3</sub> [*Williams and Long*, 1995]. However at a given relative humidity the equilibrium aqueous HNO<sub>3</sub> composition in solution is higher than that of aqueous H<sub>2</sub>SO<sub>4</sub>. For example at a relative humidity of 50 % (for  $T = 190$  K), the aqueous equilibrium HNO<sub>3</sub> molality is about 11  $m$  (41 % HNO<sub>3</sub> by weight) whereas that of aqueous H<sub>2</sub>SO<sub>4</sub> is about 6  $m$  (37 % H<sub>2</sub>SO<sub>4</sub> by weight). Thus we suggest that for the same ambient conditions, the higher H<sub>2</sub>SO<sub>4</sub> viscosity in solution may be compensated by the fact that the aqueous HNO<sub>3</sub> concentration in solution is higher. Nevertheless, our assumption is crude and future laboratory data on ice nucleation from aqueous HNO<sub>3</sub> solutions are needed for a more accurate determination of  $\Delta F_{act}$  in aqueous HNO<sub>3</sub> solutions.

The free energy term is given by

$$\Delta F_g = \frac{4}{3} \pi \sigma_{nit/ice} r_g^2 \quad (4)$$

where  $\sigma_{nit/ice}$  (dyne cm<sup>-1</sup>) is the interface energy between the ice/nitrate solution and  $r_g$  (cm) is the critical ice germ radius which is defined as [*Jensen et al.*, 1994]

$$r_g = \frac{2M_w \sigma_{nit/ice}}{\rho_{ice} \left[ L_m \ln \frac{T_f}{T} + \frac{1}{2} R(T + T_f) \ln a_w \right]} \quad (5)$$

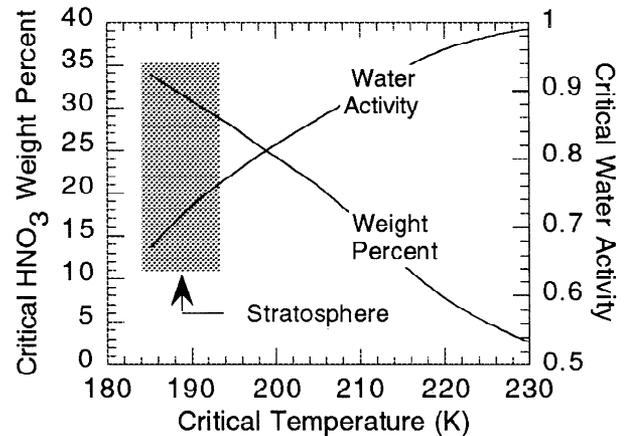
where  $M_w$  is the molecular weight of water (g.mol<sup>-1</sup>),  $\rho_{ice}$  is the ice density (g cm<sup>-3</sup>),  $L_m$  is the latent heat of ice melting

(erg mol<sup>-1</sup>),  $T_f$  is the ice melting temperature (273.15 K), and  $R$  is the universal gas constant. To derive a relation for the variation of  $\sigma_{nit/ice}$  with temperature and aerosol composition, we used the Antonoff's rule of surface tension [*Adamson*, 1990] and the laboratory data of *Granzhan and Laktionova* [1975] (See *Tabazadeh et al.* [1997b] for the derivation of this equation). This relation is given as

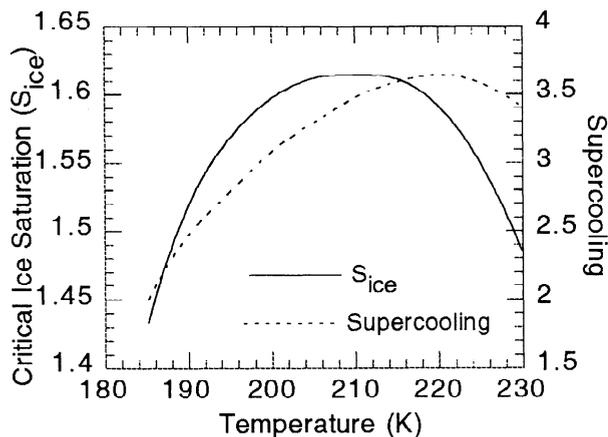
$$\sigma_{nit/ice} = 32.25 + 0.0557w_n + 0.002455w_n^2 + 0.166(T - 293.15) \quad (6)$$

### Atmospheric Applications

Using equations (1) through (6) we calculated the critical compositions and temperatures at which ice crystals will nucleate ( $J = 1$  particle<sup>-1</sup> sec<sup>-1</sup>) in a 0.2 micron aqueous HNO<sub>3</sub> droplet (Figure 1). Figure 1 illustrates that ice particles will nucleate in the stratosphere when the relative humidity with respect to water is in the range of 65 to 75 % (or  $T$  is between 185 to 190 K). This corresponds to HNO<sub>3</sub> aqueous solutions which contain between 30 to 35 % HNO<sub>3</sub> by weight. In Figure 2 the critical water activities shown in Figure 1 are converted into critical ice saturation ratios. These ice saturation ratios correspond to supercoolings of aqueous HNO<sub>3</sub> solution droplets to about 2 to 3 K below the equilibrium condensation point of ice in solution.



**Figure 1.** Variation of the nucleating aerosol composition with temperature for an aqueous HNO<sub>3</sub> solution droplet of size 0.2 micron. To obtain the results shown in this plot we set  $J$  (part<sup>-1</sup> sec<sup>-1</sup>) = 1, which is equivalent to the point at which ice will nucleate in a 0.2 micron aerosol. Also shown is the variation of the water activity over the given aerosol solution composition.



**Figure 2.** Variation of the critical ice saturation and the extent of supercooling with temperature for an aqueous  $\text{HNO}_3$  solution droplet of size 0.2 micron. This figure was obtained by converting the critical water activities shown in Figure 1 into critical ice saturation ratios.

For convenience we fitted the critical temperature of ice particle formation, from a 0.2 micron aqueous  $\text{HNO}_3$  droplet, in the stratosphere into a simple polynomial function, given as

$$T_c = 248.65 + 9.9427(\ln P) + 0.29414(\ln P)^2 \quad (7)$$

where  $P$  is the ambient water vapor concentration in units of mbar. This relation is valid over a pressure range of  $10^{-1}$  to  $10^{-5}$  mb. As described above, for the stratospheric range of water vapor pressures, the barrier to the formation of ice is about 2 to 3 K (Figure 2). In many studies the ice frost point temperature is assumed to be the critical temperature at which stratospheric aerosols would most likely freeze [Tabazadeh *et al.*, 1995, 1996; Larsen *et al.*, 1995, 1996]. In other studies nitric acid trihydrate (NAT) particle formation is suggested to occur on the surfaces of ice crystals in solution [Koop *et al.*, 1995]. For either case we suggest using equation (7) to estimate the critical temperature at which ice clouds (Type II PSCs) can form in the stratosphere instead of assuming that this critical temperature is equivalent to the ice frost point temperature.

As discussed by Toon *et al.* [1989] and Jensen *et al.* [1994], the fraction of the total number of aerosols that would freeze into ice, when temperatures drops below  $T_c$ , depends upon the cooling rate and the ambient conditions. To estimate this dependence, we have used a detailed microphysical model similar to that described by Jensen *et al.* [1994]. We set up the model with 90 size bins for each of two particle types (aqueous nitric acid aerosols and activated ice crystals) spanning the radius range from 0.005 to 80 microns. For the initial nitric acid aerosol size distribution, we used a log-normal distribution with  $N = 15 \text{ cm}^{-3}$ ,  $r = 0.092$  microns, and  $\sigma = 1.8$  [Dye *et al.*, 1992]. The partial pressure of water vapor was fixed at  $3 \times 10^{-4}$  mbar (typical for the conditions at 60 mb), and the initial temperature was set at 195 K. To calculate the freezing rate for the aqueous nitric acid aerosols, we used the expressions given above (3-6). Simulations were run with cooling rates ranging from typical synoptic scale rates (a few  $\text{K day}^{-1}$ ) to rapid cooling in lee wave clouds (up to  $1000 \text{ K day}^{-1}$ ). In each simulation, the largest aerosols froze first, and the resulting ice crystals grew by vapor deposition. As the cooling continues, more and more aerosols freeze. The fraction of aqueous nitric acid aerosols which freeze into ice crystals is plotted versus cooling rate in Figure 3. Only for the lee wave cooling rates  $> 500 \text{ K day}^{-1}$  would a large fraction of the aerosols freeze into ice crystals.

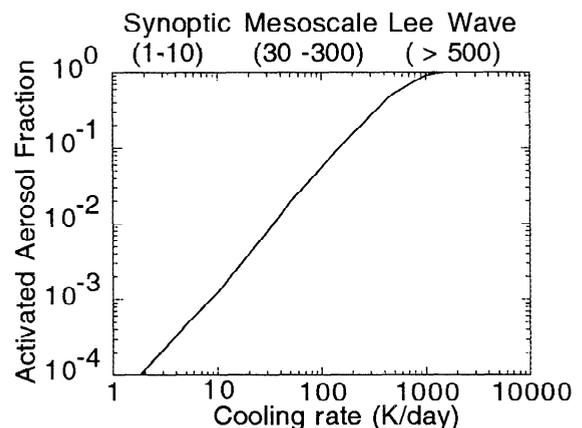
It is important to note that for a rapid cooling rate of about  $1000 \text{ K day}^{-1}$ , the  $\text{HNO}_3$  uptake over a size distribution (given above) of background sulfate aerosols is not expected to follow a smooth equilibrium uptake [Meilinger *et al.*, 1996].

In fact including the kinetics in the uptake of  $\text{HNO}_3$  for the case of a rapid cooling rate of  $1000 \text{ K day}^{-1}$ , we calculate that the majority of the background aerosols are not composed of aqueous  $\text{HNO}_3$  as we have assumed above. However due to the fact that temperature is changing very rapidly ( $1000 \text{ K day}^{-1}$ ), the effect of composition on the rate of ice formation may have very little influence on the fraction of frozen particles. For example we have performed another set of calculations assuming that the aerosols were pure  $\text{H}_2\text{SO}_4$  and we obtained a curve which closely matched the results shown in Figure 3 for aqueous  $\text{HNO}_3$ . Since the fraction of frozen ice particles remains the same for both aqueous  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  solutions, we conclude that this fraction will not change significantly with the variations in the aerosol composition caused by the kinetics of the  $\text{HNO}_3$  uptake.

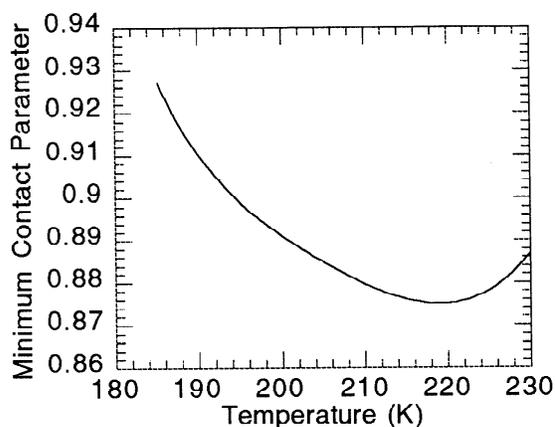
It is clear from the above discussion that in cold lee waves the majority of the background aerosols may freeze into ice particles. However, the question of whether ice formation in such droplets would result in the crystallization of  $\text{HNO}_3$  has not been resolved yet. Some recent laboratory work suggest that, in aqueous  $\text{H}_2\text{SO}_4$  droplets, ice nucleation in solution may not result in the crystallization of  $\text{H}_2\text{SO}_4$  [Anthony *et al.*, 1995]. Other laboratory work on aqueous  $\text{H}_2\text{SO}_4$  solution droplets suggest that sulfate in the solution, near the ice point, would freeze into an octahydrate phase instead of the commonly assumed tetrahydrate (SAT) phase [Imre *et al.*, 1997].

Currently only a few laboratory works are available on the crystallization of  $\text{HNO}_3$  from aqueous  $\text{HNO}_3$  films [Tolbert *et al.*, 1992; Middlebrook *et al.*, 1996; Tisdale *et al.*, 1997]. In those experiments, ice was either already present or crystallized as the films were heated, and subsequent warming caused crystallization of NAT prior to evaporation. In such film experiments due to the presence of a substrate, the observed  $\text{HNO}_3$  crystallization rates may not be applicable to what may occur in a small micron-sized aqueous  $\text{HNO}_3$  droplet. However, from what is known of the aqueous  $\text{H}_2\text{SO}_4$  acid system ice nucleation in droplets may or may not result in the crystallization of  $\text{HNO}_3$ . Further it is more likely that a dilute  $\text{HNO}_3/\text{H}_2\text{O}$  solid phase would form in the solution instead of the thermodynamically stable NAT phase since the aqueous  $\text{HNO}_3$  composition at the ice nucleation point of the solution is very dilute in  $\text{HNO}_3$  (see Figure 1). This hypothesis agrees with studies done on many other systems of aqueous particles in which the first phases to nucleate in such particles are seldom the phases that one would expect from the bulk phase thermodynamics [Tang *et al.*, 1995].

More laboratory work is needed to gain insight into how ice crystal formation in an aqueous solution may trigger the crystallization of  $\text{HNO}_3$  in solution. Perhaps the most desirable laboratory work would be to follow up a cycle of ice crystal nucleation from an aqueous solution by a subsequent warming of the droplet. The warming should be continued until



**Figure 3.** The total fraction of nucleated aerosols as a function of cooling rate. Typical synoptic, mesoscale and lee wave cooling rates are shown on the top of the chart.



**Figure 4.** Variation of the heterogeneous contact parameter with temperature. To obtain the results shown in this figure we used the water activities and temperatures shown in Figure 1 and varied the contact parameter in a gas phase heterogeneous nucleation code until the nucleation rate was identical to that of the homogeneous freezing. Thus for contact parameters lower than those shown homogeneous nucleation freezing would occur before ice nucleation by vapor deposition is possible and vice versa (see text for more detail).

the ice is evaporated off and the state of the  $\text{HNO}_3$  left behind in the aerosol can then be studied by various laboratory techniques [Anthony *et al.*, 1995; Bertram *et al.*, 1996].

We also performed heterogeneous gas phase nucleation calculations to compare the barrier of ice formation between homogeneous freezing nucleation and gas phase vapor deposition on a solid substrate. For our heterogeneous gas phase nucleation calculations we used the formulation outlined by Toon *et al.* [1989] for PSCs which is based on the work of Fletcher *et al.* [1958]. To obtain the contact parameters given in Figure 4, we varied the contact parameter in a heterogeneous nucleation code until the nucleation rate of ice formation on a solid substrate equaled the nucleation rate of ice formation by homogeneous freezing from an aqueous  $\text{HNO}_3$  droplet of size 0.2 micron. Figure 4 illustrates that if gas phase vapor deposition is to compete with homogeneous freezing, then the contact parameter between the preexisting solid substrate and ice must be greater than 0.9 for temperatures less than 192 K. It is unlikely that solid particles with such high contact parameters ( $> 0.9$ ) exist in the stratosphere. Hence we suggest that ice formation in the stratosphere would probably occur by homogeneous freezing of ice from a nearly aqueous  $\text{HNO}_3$  solution. However if some of the aqueous particles contain solid cores, then heterogeneous freezing nucleation can occur at higher temperatures in such droplets as compared to our estimates of homogeneous freezing nucleation [Jensen and Toon, 1997].

## Summary

In this paper we outlined an algorithm for ice nucleation from an aqueous  $\text{HNO}_3$  solution droplet which can be used to predict the occurrence of Type II PSCs in the stratosphere. We showed that ice nucleation in the stratosphere occurs only when ambient temperatures drop by about 2 to 3 K below the ice frost point. Further microphysical calculations suggest that freezing of nearly all the particles as ice crystals can occur in cold lee waves. However, the question of whether ice nucleation in a droplet would trigger the crystallization of either  $\text{HNO}_3$  or  $\text{H}_2\text{SO}_4$  in the aerosol remains open at this point. We also showed that solid ice nuclei with relatively high contact parameters are needed in order for a gas phase heterogeneous nucleation mechanism to compete with homogeneous freezing nucleation of ice, except for the case of heterogeneous freezing nucleation.

**Acknowledgments.** We thank Ann Middlebrook for helpful discussions. This research was completed while A. Tabazadeh held an NRC/NASA Postdoctoral Fellowship.

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(Received March 25, 1997; Revised May 16, 1997; accepted June 19, 1997)