

The effect of nitric acid uptake on the deliquescence and efflorescence of binary ammoniated salts in the upper troposphere

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[1] Thermodynamic equilibrium model calculations are used to show that HNO_3 can lower the relative humidity barrier to deliquesce binary ammoniated salts in the upper troposphere, particularly in aerosol solutions with an $(\text{NH}_4)_2\text{SO}_4$ composition. Also in the case of $(\text{NH}_4)_2\text{SO}_4$ or NH_4HSO_4 there is no abrupt change in the physical state of the thermodynamic system (instantaneous change of a dry salt particle into an aqueous solution) at the deliquescent point, which is typical for such a phase transition. Model results show that HNO_3 dissolution in ammoniated aerosol solutions can prevent the efflorescence of $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 salts in favor of $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ (letovicite) crystallization. Future laboratory experiments, where binary ammoniated salts are studied at cold temperatures in the presence of both HNO_3 and H_2O , are needed to confirm the results of our model calculations. **INDEX TERMS:** 0305 Atmospheric Composition and Structure: Aerosols and Particles (0345, 4801); 0320 Atmospheric Composition and Structure: Cloud Physics and Chemistry; 0399 Atmospheric Composition and Structure: General or Miscellaneous

1. Introduction

[2] Aerosols impact the Earth's climate and chemistry [Ravishankara, 1997]. Both the ice nucleating properties and heterogeneous reactivity of aerosols in the atmosphere are affected by their solution phase and composition. A comprehensive data set on the chemical composition and phase of aerosols in the upper troposphere is currently lacking. Observations from limited aircraft data indicate that comparable amounts of ammonium and sulfate ions may be present in upper tropospheric aerosol solutions [Talbot *et al.*, 1996, 1998]. In most bulk phase aircraft filter samples the ammonium ion mixing ratio in the aerosol is often shown to be sufficient to fully or partially neutralize the sulfate ion [Tabazadeh *et al.*, 1998].

[3] Up to now the deliquescence and efflorescence relative humidities of binary ammoniated salts have been measured in the laboratory in the absence of gas phase nitric acid [Imre *et al.*, 1997; Xu *et al.*, 1998; Onasch *et al.*, 1999; Cziczo and Abbatt, 1999]. Thus far only Brooks *et al.* [2002] have shown that mixtures of ammonium sulfate and organic acids can deliquesce at lower relative humidities than pure ammonium sulfate. Similarly, here we use a thermodynamic electrolyte model [Clegg *et al.*, 1998] to examine how HNO_3 , which is abundant in the atmosphere, can affect the deliquescence and efflorescence properties of binary salts in the upper troposphere.

2. Nitric Acid Uptake by Binary Ammoniated Salts

2.1. Deliquescence

[4] Traditionally the deliquescence relative humidity (DRH) of a binary salt is defined as the relative humidity at which a dry salt

particle instantaneously turns into an aqueous solution droplet. In fact many laboratory observations show that binary salts do abruptly change phase at a fixed RH, known as the DRH [Tang, 1996; Imre *et al.*, 1997; Xu *et al.*, 1998; Onasch *et al.*, 1999; Cziczo and Abbatt, 1999]. However, in the atmosphere such a definition is too simple for two reasons. First, in the atmosphere a dry salt particle is exposed to other gaseous components, besides just H_2O which determines the RH. For example, in the case of HNO_3 , we have shown that it is highly soluble in aqueous $(\text{NH}_4)_2\text{SO}_4$ at cold temperatures [Lin and Tabazadeh, 2001]. Also, H^+ ions from the HNO_3 dissolution process can interact in an $(\text{NH}_4)_2\text{SO}_4$ solution to produce $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ (letovicite) [Tabazadeh and Toon, 1998]. Second, at low temperatures, the equilibrium composition of a dry binary salt at low relative humidity may be different than that of a pure salt, which may exist at room temperature. For example, the thermodynamic model of Clegg *et al.* [1998] predicts that at low temperatures (<230 K), in the presence of gas phase HNO_3 , a pure dry $(\text{NH}_4)_2\text{SO}_4$ particle cannot exist in the upper troposphere. The model predicts that an equilibrium composition of a dry salt particle with the stoichiometric ratio of $(\text{NH}_4)_2\text{SO}_4$ will exist as a mixture of $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ (letovicite) and NH_4NO_3 . The mole ratio of ammonium to sulfate ion is the same for both a pure dry $(\text{NH}_4)_2\text{SO}_4$ particle and a dry salt mixture containing one mole of $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ and one mole of NH_4NO_3 .

[5] Below we describe in detail how a dry ammoniated salt particle may deliquesce in the upper troposphere in the presence of both H_2O and HNO_3 , using the thermodynamic electrolyte model of the $\text{NH}_3\text{-H}_2\text{SO}_4\text{-HNO}_3\text{-H}_2\text{O}$ system [Clegg *et al.*, 1998]. Because thermodynamic systems of binary ammoniated aerosols are complicated in the upper troposphere, we will adopt a new definition for the deliquescent point. In our definition, the deliquescence occurs at a fixed RH where the aqueous solution phase will first appear. Also, for some salt compositions, the deliquescent point can no longer be viewed as an abrupt change in the physical state of the system, i.e. salt instantaneously changing into an aqueous solution phase. For example, as shown below, for $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 systems, the state of the particle will remain mixed (salt plus solution phase) both at the deliquescent point and at RHs higher than this point.

2.1.1. $(\text{NH}_4)_2\text{SO}_4$. [6] In Figure 1a the variation of the DRH is shown for the $(\text{NH}_4)_2\text{SO}_4$ system both in the presence and absence of gas phase HNO_3 . The HNO_3 concentration used ranges from zero (simulating conditions used in laboratory experiments [Imre *et al.*, 1997; Xu *et al.*, 1998; Onasch *et al.*, 1999; Cziczo and Abbatt, 1999] to background (100 pptv) [Singh *et al.*, 1996] and polluted (up to 2 ppbv) [Laaksonen *et al.*, 1997] levels in the upper troposphere. The green line shows the standard DRH where the gas phase HNO_3 is set to zero in the calculations. The black lines show the effect on the DRH once HNO_3 is introduced into the gas phase. For RHs below the S line in Figure 1a, dry $(\text{NH}_4)_2\text{SO}_4$ will exist as a mixture of NH_4NO_3 and letovicite (see above). It is clear from the results shown in Figure 1a that HNO_3 can strongly affect the DRH behavior of the $(\text{NH}_4)_2\text{SO}_4$ system. The lines labeled as S show the RH at which the aqueous solution phase will first appear. Compared to the standard green line, the presence of HNO_3 can

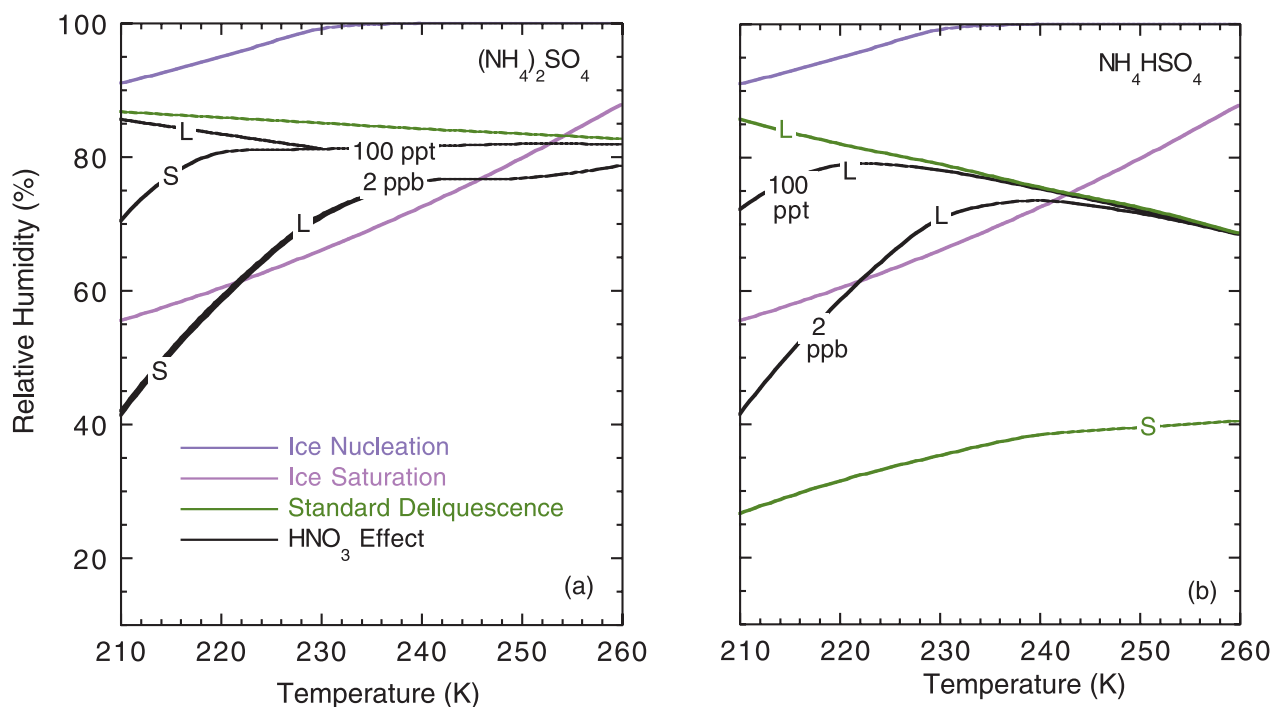


Figure 1. The effect of HNO_3 uptake on the deliquescence of (a) $(\text{NH}_4)_2\text{SO}_4$ and (b) NH_4HSO_4 . The ice nucleation and saturation lines are also marked on the plot. We used the *Tabazadeh et al.* [2000] ice nucleation line for a 0.2 micron aerosol particle. The green lines show the standard DRH behavior in the absence of HNO_3 . The black lines show the effect of HNO_3 uptake for a gas phase mixing ratio of ~ 100 pptv and 2 ppbv. Lines marked as S show the point where the aqueous solution phase will first appear. The L lines mark the point where letovicite will fully dissolve in the aqueous solution. Between the S and L lines the equilibrium system is in a mixed state. See text for more detail. Model calculations were performed using a fixed binary salt concentration of 10^{-9} mole m^{-3} (~ 100 ppt at 200 mb) for both panels [Talbot et al., 1998]. The HNO_3 concentration was set to zero for the standard calculations (green lines) and was varied from 1 (~ 100 ppt at 200 mb) to 20 (~ 2 ppbv at 200 mb) $\times 10^{-9}$ moles m^{-3} in the HNO_3 simulations. Note that in order to obtain the results shown neither H_2SO_4 nor HNO_3 hydrates were allowed to form during the model simulations.

lower the RH of $(\text{NH}_4)_2\text{SO}_4$ deliquescence. The more HNO_3 there is in the gas phase, the stronger is its effect in the lowering of the standard DRH line. For example, at 210 K, the standard DRH (green line) is lowered from 87 to 71 and 43% RH in the presence of 100 ppt and 2 ppv HNO_3 , respectively. When the solution phase will first appear (S line in Figure 1a), the thermodynamic system is composed of a mixture of an aqueous solution, letovicite and NH_4NO_3 . Letovicite will persist in this aqueous solution until the RH reaches the line marked as L in Figure 1a. At this point, letovicite will fully dissolve in the aqueous solution and the thermodynamic equilibrium system left behind is then composed of a mixture of an aqueous solution plus NH_4NO_3 salt. For RHs between the S and L lines the thermodynamic state of the system is composed of an aqueous solution plus letovicite and NH_4NO_3 . For simplicity we have not shown a line where NH_4NO_3 salt will fully dissolve in the aqueous solution because NH_4NO_3 can persist in this solution near 95% RH (for $T < 230$ K). Under such humid conditions ice will most likely nucleate in the aqueous solution (see the blue line in Figure 1a). After ice formation the RH will decrease to the point of ice saturation (see the purple line in Figure 1), where NH_4NO_3 can no longer dissolve in the left over aqueous solution. It is important to note that if NH_4NO_3 cannot crystallize in upper tropospheric aerosol solutions under any circumstances [Cziczo and Abatt, 2000], then the state of an $(\text{NH}_4)_2\text{SO}_4$ aerosol will always be mixed (letovicite plus an aqueous solution) at RHs below the L Line, and completely aqueous at RHs above the L line.

2.1.2. NH_4HSO_4 . [7] In Figure 1b the change in the DRH of NH_4HSO_4 due to the presence of gas phase HNO_3 is shown. Since the NH_4HSO_4 system carries an H^+ ion, letovicite can form in this

system at cold temperatures even in absence of gas phase HNO_3 [Yao et al., 1999]. To better understand the DRH behavior of the NH_4HSO_4 in the presence of HNO_3 , we first briefly describe the standard behavior of this system at cold temperatures in the absence of HNO_3 . Below the green line (labeled as S), the *Clegg et al.* [1998] model predicts that NH_4HSO_4 can exist as a pure dry salt particle. At the S line in Figure 1b an aqueous solution phase will first appear, and the thermodynamic state of the system across this line is composed of an aqueous solution plus letovicite. Note that even though the dry equilibrium state of the particle is NH_4HSO_4 , the salt in solution co-existing with the aqueous phase across the S line is letovicite not NH_4HSO_4 . Letovicite will then fully dissolve in this aqueous solution across the line marked as L in Figure 1b. For RHs between the S and L lines the equilibrium state of the system is composed of an aqueous solution plus letovicite.

[8] HNO_3 will affect the NH_4HSO_4 system less than $(\text{NH}_4)_2\text{SO}_4$ because it is only scarcely soluble in NH_4HSO_4 under upper tropospheric conditions [Lin and Tabazadeh, 2001]. Nevertheless, the HNO_3 effect is significant at low temperatures, particularly when large amounts of HNO_3 are present in the gas phase. When HNO_3 is introduced into the gas phase, due to its low solubility, it will not affect the point where the aqueous solution phase will first appear. In other words, the S lines for the two HNO_3 lines shown in Figure 1b lie on top of the green line marked as S for the standard case. Thus, whether HNO_3 is present in the gas phase or not will not affect the point where NH_4HSO_4 will first turn into an aqueous solution-letovicite mixture. However, the presence of HNO_3 will cause letovicite to dissolve in the aqueous solution at a lower RH than that

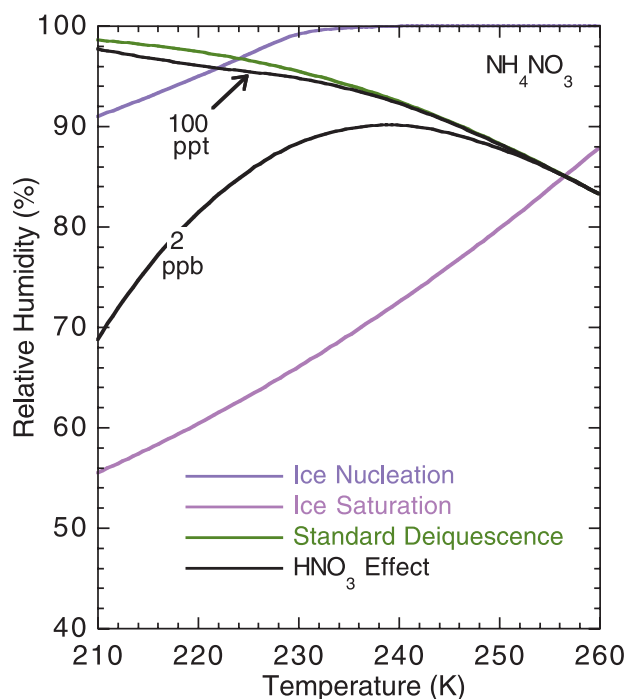


Figure 2. The effect of HNO_3 uptake on the deliquescence of NH_4NO_3 . See the caption of Figure 1 for model assumptions used and description of various lines plotted.

predicted for the standard case (green line), where HNO_3 is absent. For example, at 210 K, letovicite will fully dissolve in the aqueous solution near 86 and 42% RH when HNO_3 mixing ratio is raised from 0 to 2 ppbv, respectively. Thus the RH range over which letovicite can persist in the aqueous solution will shrink as HNO_3 gas phase concentration is increased in the atmosphere.

2.1.3. NH_4NO_3 . [9] Since new salts, such as letovicite, cannot form in the binary NH_4NO_3 system, the effect of HNO_3 on the DRH is limited (see Figure 2). The standard DRH line (green line) is lowered when HNO_3 is introduced and the effect becomes stronger as HNO_3 concentration is increased in the gas phase. For example, at 210 K, the effect of HNO_3 uptake on the DRH of NH_4NO_3 is negligible for typical background levels (~ 100 ppt) of HNO_3 . However, at 210 K, the standard DRH (green line) is lowered from 98 to 69% when gas phase HNO_3 mixing ratio is set to 2 ppbv. Also, unlike the $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 systems, the deliquescence of NH_4NO_3 in the presence of HNO_3 should still occur via an abrupt phase transition step.

2.2. Efflorescence

[10] Exposure of ammoniated salts to nitric acid can also affect the efflorescence (crystallization) relative humidity (ERH) of binary ammoniated salts in the upper troposphere. Figure 3 illustrates how saturation ratios (SRs) of $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 change with relative humidity and HNO_3 concentration at 230 K. A salt can form and persist in an aqueous solution when its SR equals or exceeds one. NH_4NO_3 is omitted in this discussion because NH_4NO_3 is the only salt that can form in the NH_4NO_3 - HNO_3 system.

[11] Horizontal lines in Figure 3 mark the saturation requirements for crystallizing $(\text{NH}_4)_2\text{SO}_4$ or letovicite $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ (for NH_4HSO_4 , the ERH is below 5%) in an aqueous solution droplet at room temperature. The lines are drawn by converting the measured ERH (both $\sim 39\%$ [Tang, 1996]) of the two salts at room temperature into salt saturation ratios using the model of Clegg

et al. [1998]. As expected, $(\text{NH}_4)_2\text{SO}_4$ SR in solution decreases (salt is less saturated) with increasing amounts of HNO_3 , making it more difficult for $(\text{NH}_4)_2\text{SO}_4$ to effloresce (crystallize) in solution as compared to the case where HNO_3 is absent. For NH_4HSO_4 SRs remain roughly the same for all HNO_3 concentration levels, mainly because HNO_3 is only scarcely soluble in NH_4HSO_4 [Lin and Tabazadeh, 2001]. However, $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ is highly saturated in

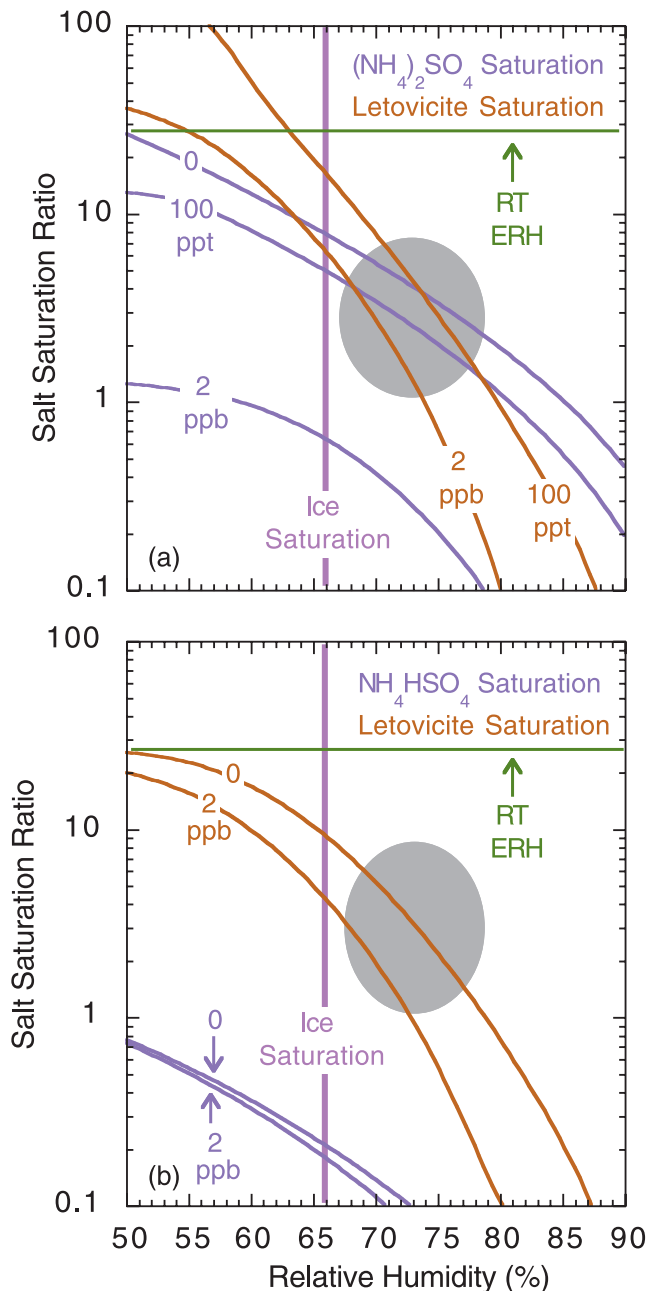


Figure 3. The effect of HNO_3 uptake on the efflorescence of (a) $(\text{NH}_4)_2\text{SO}_4$ and (b) NH_4HSO_4 aqueous solutions at 230 K. The variations in salt saturation ratio (SR) as a function of RH are also shown. Room temperature ERHs and ice saturation lines are also marked. The shaded area marks the region where both ice and ammoniated salts are saturated in the aqueous solution. See text for more detail. The model conditions used for binary salts and various HNO_3 concentrations are described in the caption of Figure 1. In order to obtain salt SRs we assumed that the solution was supercooled and therefore neither salts nor ice were allowed to form during the simulations.

both solutions of $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 . As shown in Figure 3, SR of letovicite in solution is higher than both binary salts, indicating that the likelihood for letovicite to crystallize is favored over the binary salts. Thus, $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 probably cannot effloresce in upper tropospheric aerosols once letovicite forms in solution. Calculations performed at temperatures of 230 ± 15 K (not shown) indicate a similar effect of favoring letovicite formation over the binary salts.

[12] In ice saturated regions letovicite can still persist in aqueous solutions because its SR exceeds one (shaded areas in Figure 3). A few studies have suggested that ice may heterogeneously nucleate on solid letovicite surfaces in such a mixed-phase aerosol system [Tabazadeh and Toon, 1998; Zuberi et al., 2001]. Here, we have shown that nitric acid uptake would allow for a pure $(\text{NH}_4)_2\text{SO}_4$ particle to exist as a mixed-phase aerosol in the upper troposphere. For the NH_4HSO_4 system, the state of the aerosol will also be often mixed at cold temperatures. Thus it is possible for ice formation, from both $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 , to occur via a heterogeneous nucleation step in the upper troposphere.

3. Summary

[13] In this paper we have shown that exposing binary ammoniated salts to nitric acid can affect their DRH behavior. Also, the deliquescence of $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 systems in the upper troposphere cannot occur via an abrupt phase transition step, as typically seen in the laboratory near room temperature in the absence of gas phase HNO_3 . In addition, binary ammoniated salts containing sulfate ions are most likely converted to letovicite $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ in the upper troposphere, which can then persist in aerosol solutions that are saturated with respect to ice. Letovicite crystallization in solution can efficiently suppress the efflorescence of both $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 in upper tropospheric aerosol solutions. Thus, it is unlikely for crystalline phase $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 to exist in the environment of the upper troposphere. Future laboratory experiments on the deliquescence and efflorescence properties of binary ammoniated salts in the presence of HNO_3 are highly desirable to confirm the results of our calculations.

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