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Formation of binary ion clusters from polar vapours: Effect of the dipole-charge interaction

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Abstract

Formation of binary cluster ions from polar vapours is considered. The effect of vapour polarity on the size and composition of the critical clusters is investigated theoretically and a corrected version of classical Kelvin-Thomson theory of binary ion-induced nucleation is derived. The model predictions of the derived theory are compared to the results given by classical binary homogeneous nucleation theory and ion-induced nucleation theory. The calculations are performed in wide range of the ambient conditions for a system composed of sulfuric acid and water vapour. It is shown that dipole-charge interaction significantly decreases the size of the critical clusters, especially under the atmospheric conditions when the size of critical clusters is predicted to be small.

1. Introduction

Formation of ultrafine aerosols has received increasing attention in the last few decades due to its importance for atmospheric physics and chemistry, chemical technology and health research. The possible role of air ions in aerosol formation, which was intensively studied during seventies and earlier eighties (e.g. Mohnen, 1971; Castleman et al., 1978; Arnold, 1980; Hamill et al., 1982), has received renewed attention in recent years (e.g. Yu and Turco, 2000; Carslaw et al., 2002; Eichkorn et al., 2002; Yu, 2002, 2003). Classical theory of ion-induced nucleation (IIN) (e.g. Hamill et al., 1982; Raes et al., 1986; Laakso et al., 2002) treats the cluster formation using capillary approximation and it accounts for the charge effect on the pressure in the condensed phase only. However, the electrical field influences not only the particle but also the surrounding gaseous media. Recent studies showed that the interaction of polar vapour molecules with the electrical field of charged particles may be important for the formation of small ion clusters. Nadykto et al. (2003) considered the ion- induced formation of single-component particle and they concluded that the contribution of the dipole-charge attraction potential to the size of the ion clusters is significant, when polar vapours are

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involved in the nucleation process.

The purpose of this paper is to study the effect of dipole-charge interaction on the formation of binary cluster ions. We will derive the generalized Kelvin-Thomson equation accounting for vapour polarity, calculate the critical size of binary sulfuric acid-water ion clusters and compare our model predictions with the results of the ealier theories.

2. Model

In the classical binary IIN theory (e.g. Hamill et al., 1982; Raes et al., 1986; Laakso et al., 2002) in the prevailing temperature T and vapor pressures of two condensing components a and b, the critical size of binary cluster ion is determined from the Kelvin-Thomson equation (e.g. Laakso et al., 2002),

$$\ln S' = \frac{\overline{V}}{kT}\left[\frac{4\sigma}{D'_p} - \left(\frac{1}{\varepsilon_g} - \frac{1}{\varepsilon_r}\right)\frac{(qe_0)^2}{2\pi^2\varepsilon_0 D'^4_p}\right], \tag{1}$$

where $S' = S_a^{1-x_b}S_b^{X_b}$, $\overline{V} = (1 - X_b)v_a + X_bv_b$, $\frac{\pi D'^3_p}{6} = \rho = n_am_a + n_bm_b$. Here S' is the generalized saturation ratio, S_a and S_b are the saturation ratios for component a and b, respectively, $\overline{V}$ is the average molecular volume, v_a and v_b are the partial molecular volumes for components a and b, respectively, n_a and n_b are the number of molecules in the particle for components a and b, respectively, m_a and m_b are the molecule mass of components a and b, respectively, q is the number of the charges in the cluster, e_0 is the elementary charge, σ is the surface tension, ε_r is the relative permittivity of particle, ε_g is the relative permittivity of the condensable vapour, ε_0 is the vacuum permittivity, k is the Boltzman constant, ρ is the particle/cluster density, X_a and X_b are molar fractions for components a and b, respectively, and D'_p is the diameter of the cluster. The composition of the charged particle is decided by the following equation

$$\frac{v_a}{\Delta\mu_a} = \frac{v_b}{\Delta\mu_b}, \tag{2}$$

where $\Delta\mu_i = \mu_{iL} - \mu_{ig}$ is the chemical potential change from gas phase (μ_{ig}) to condesed or liquid phase (μ_{iL}) of component $i (i = a, b)$. In such a binary system, the Gibbs free energy can be expressed by the following equation

$$\Delta G = n_a \Delta\mu_a + n_b \Delta\mu_b + \sigma A + \frac{q^2 e_0^2}{8\pi\varepsilon_0}\left(\frac{1}{\varepsilon_g} - \frac{1}{\varepsilon_r}\right)\left(\frac{1}{r} - \frac{1}{r_0}\right),\tag{3}$$

5 where r is the cluster radius, A is the cluster surface area, and r_0 is the radius of the core ion. Applying extreme condition for function ΔG at constant temperature and pressure,

$$d\Delta G = 0,\tag{4}$$

we get, after taking into account the Gibbs-Duhem identity (Renninger et al., 1981), the
10 following set of differentiation equations,

$$(\mu_{aL} - \mu_{ag}) - \left(n_a\frac{\partial\mu_{ag}}{\partial n_a} + n_b\frac{\partial\mu_{bg}}{\partial n_a}\right) + 8\pi r\sigma\frac{\partial r}{\partial n_a} - \frac{q^2 e_0^2}{8\pi\varepsilon_0}\left(\frac{1}{\varepsilon_g} - \frac{1}{\varepsilon_r}\right)\frac{1}{r^2}\frac{\partial r}{\partial n_a} = 0,\tag{5}$$

$$(\mu_{bL} - \mu_{bg}) - \left(n_a\frac{\partial\mu_{ag}}{\partial n_b} + n_b\frac{\partial\mu_{bg}}{\partial n_b}\right) + 8\pi r\sigma\frac{\partial r}{\partial n_b} - \frac{q^2 e_0^2}{8\pi\varepsilon_0}\left(\frac{1}{\varepsilon_g} - \frac{1}{\varepsilon_r}\right)\frac{1}{r^2}\frac{\partial r}{\partial n_b} = 0.\tag{6}$$

The interdependence between n_a, n_b and r is expressed as

$$\frac{4}{3}\mu r^3\rho = n_a m_a + n_b m_b + M_0.\tag{7}$$

15 where M_0 is the mass of core ion. In the electrical field of the charged cluster/particle, the difference between chemical potentials of the polar molecules in the condensed phase and in the gas phase is given by (e.g. Nadykto et al., 2003)

$$\mu_{iL} - \mu_{ig} = -kT\left[\ln\left(\frac{A_{ig\infty}}{A_{iL}}\right) + \ln\left(\frac{p_{ig}}{p_{i\infty}}\right)\right].\tag{8}$$

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where A_{il} is activity of component i in the condensed phase, $A_{ig\infty}$ is activity of component i in the gas phase, p_{ig} is the vapour pressure over the particle surface, $p_i\infty$ is the ambient vapour pressure, and $\ln\left(\frac{p_{ig}}{p_{i\infty}}\right)$ described by the following equation

$$\ln\left(\frac{p_{ig}}{p_{i\infty}}\right) = \frac{\alpha_i(qe_0)^2}{32\pi^2\varepsilon_0^2 r^4 kT} + \ln\left[\frac{\sinh\left(\frac{qe_0 l_i}{4\pi\varepsilon_0 kTr^2}\right)}{\frac{qe_0 l_i}{4\pi\varepsilon_0 kTr^2}}\right]. \quad (9)$$

5 where $\sinh(z) = [\exp(z) + \exp(-z)/2$, l_i is the dipole moment of component i and α_i is the polarizability of component i. Equation (9) describes the effect of the molecular dipole-charge interaction on the vapour pressure in the vicinity of the charged particle/cluster that appears due to the attraction of the polar vapour molecules by the electrical field of the charged particle/cluster.

10 Inserting Eq. (8) into Eqs. (5) and (6), and after some algebra, we get

$$-kT\left[\ln\left(\frac{A_{ag\infty}}{A_{aL}}\right) + \ln\left(\frac{p_{ag}}{p_{a\infty}}\right)\right] - \left[\frac{\partial\left(\ln\left(\frac{P_{ag}}{p_{a\infty}}\right)\right)}{\partial r}n_a + \frac{\partial\left(\ln\left(\frac{P_{bg}}{P_{b\infty}}\right)\right)}{\partial r}n_b\right]\frac{\partial r}{\partial n_a}$$

$$+8\pi r\sigma\frac{\partial r}{\partial n_a} - \frac{q^2 e_0^2}{8\pi\varepsilon_0}\left(\frac{1}{\varepsilon_g} - \frac{1}{\varepsilon_r}\right)\frac{1}{r^2}\frac{\partial r}{\partial n_a} = 0 \quad (10)$$

$$-kT\left[\ln\left(\frac{A_{ag\infty}}{A_{aL}}\right) + \ln\left(\frac{p_{ag}}{p_{a\infty}}\right)\right] - \left[\frac{\partial\left(\ln\left(\frac{P_{ag}}{p_{a\infty}}\right)\right)}{\partial r}n_a + \frac{\partial\left(\ln\left(\frac{P_{bg}}{P_{b\infty}}\right)\right)}{\partial r}n_b\right]\frac{\partial r}{\partial n_b}$$

$$+8\pi r\sigma\frac{\partial r}{\partial n_b} - \frac{q^2 e_0^2}{8\pi\varepsilon_0}\left(\frac{1}{\varepsilon_g} - \frac{1}{\varepsilon_r}\right)\frac{1}{r^2}\frac{\partial r}{\partial n_b} = 0. \quad (11)$$

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Now we add the 2nd line of Eq. (11) to 2nd line of Eq. (10) to obtain

$$-kT\left[\ln\left(\frac{A_{ag\infty}}{A_{aL}}\right) + \ln\left(\frac{p_{ag}}{p_{a\infty}}\right) + \ln\left(\frac{A_{bg\infty}}{A_{bL}}\right) + \ln\left(\frac{p_{bg}}{P_{b\infty}}\right)\right]$$

$$-\left[\frac{\partial\left(\ln\left(\frac{p_{ag}}{p_{a\infty}}\right)\right)}{\partial r}n_a + \frac{\partial\left(\ln\left(\frac{p_{bg}}{p_{b\infty}}\right)\right)}{\partial r}n_b\right]\left(\frac{\partial r}{\partial n_a} + \frac{\partial r}{\partial n_b}\right) +$$

$$8\pi r\sigma\left(\frac{\partial r}{\partial n_a} + \frac{\partial r}{\partial n_b}\right) - \frac{q^2 e_0^2}{8\pi\varepsilon_0}\left(\frac{1}{\varepsilon_g} - \frac{1}{\varepsilon_r}\right)\frac{1}{r^2}\left(\frac{\partial r}{\partial n_a} + \frac{\partial r}{\partial n_b}\right) = 0 \quad (12)$$

and, then, multiply both sides of Eq. (10) by $\left(\frac{\partial n_a}{\partial r}\right)$ and both sides Eq. (11) by $\left(\frac{\partial n_b}{\partial r}\right)$, and subtract the equations obtained to get

$$\left[\ln\left(\frac{A_{ag\infty}}{A_{aL}}\right) + \ln\left(\frac{p_{ag}}{p_{a\infty}}\right)\right]\frac{\partial n_a}{\partial r} = \left[\ln\left(\frac{A_{bg\infty}}{A_{bL}}\right) + \ln\left(\frac{p_{bg}}{p_{b\infty}}\right)\right]\frac{\partial n_b}{\partial r}. \quad (13)$$

In prevailing temperature and saturation ratios of the components a and b, solution to the set of Eqs. (9), (12) and (13) gives us the numbers of molecules of components a and b in the cluster and the cluster size. As may be seen from Eqs. (12) and (13), Eq. (12) reduces to Eq. (1) and Eq. (13) reduces to Eq. (2), when the dipole-charge interaction is neglected. While the position of local maximum or minimum in classical theory of IIN is independent of the size of the core ion, the presented model includes this dependence explicitly.

Expressions for $\left(\frac{\partial r}{\partial n_i}\right)$ and $\frac{\partial\left[\ln\left(\frac{p_{ig}}{p_{i\infty}}\right)\right]}{\partial r}(i = a, b)$ needed to solve the set of Eqs. (9), (12) and (13) are given by Eqs. (14) and (15), respectively,

$$\frac{\partial n_i}{\partial r} = \frac{4\pi r^2 \rho}{m_i}, \quad (14)$$

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$$\left(\frac{\partial \left[\ln \left(\frac{p_{ig}}{p_{i\infty}} \right) \right]}{\partial r} \right) = \frac{d}{dr} \left[\frac{\alpha_1 (qe_0)^2}{32\pi^2 \varepsilon_0^2 r^4 kT} = \ln \left[\frac{\sinh \left(\frac{qe_0 l_i}{4\pi\varepsilon_0 kT r^2} \right)}{\frac{qe_0 l_i}{4\pi\varepsilon_0 kT r^2}} \right] \right] =$$

$$\frac{-4}{r} \left(\frac{\alpha_i (qe_0)^2}{32\pi^2 \varepsilon_0^2 r^4 kT} \right) + \left(\frac{-2}{r} \right) \left(\frac{qe_0 l_i}{4\pi\varepsilon_0 kT r^2} \right) L \left(\frac{qe_0 l_i}{4\pi\varepsilon_0 kT r^2} \right), \qquad (15)$$

where $L(z) = \left[\frac{e^z + e^{-z}}{e^z - e^{-z}} \right] - \frac{1}{z}$ is the Langevin function.

The derived model can be considered as a generalization of the classical binary IIN theory because it not only considers all the mechanisms involved in classical binary IIN but also include the effect of the dipole-charge interaction neglected in the classical binary IIN theory .

3. Results and discussion

Calculations were performed using Eqs. (12)–(13) for binary sulphuric acid-water vapour gas mixture. Binary clusters are assumed to be singly charged. Values of input parameters are adopted from CRC Handbook of Chemistry and Physics (2002), Kulmala et al. (1998) and Myhre et al. (1998). Figures 1–4 show the comparisons of the cluster sizes as functions of ambient temperature (T), relative humidity (RH), and the concentration of sulfuric acid vapour calculated from Eqs. (1)–(2) $q = 1$ (IIN) and $q = 0$ (BHN, binary homogeneous nucleation), and Eqs. (12) and (13) (this study).

As may be seen from Figs. 1–4, dipole-charge interaction significantly influences the formation of small cluster ions, reducing the number of molecules in the critical cluster and, consequently, decreasing the critical size. Difference between results given by the considered theories rises as the cluster size decreases. For small clusters, the difference in the numbers of molecules in the critical cluster may be as big as more than 2 times. The deviation between IIN theory and present theory rises as the relative

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humidity and sulfuric acid concentration grow. The contribution of the Thomson effect was found to be smaller than that of the dipole-charge interaction, which is essential when highly polar vapours are nucleating. As may be seen from Figs. 1–4, the classical Kelvin-Thomson equation overestimates significantly the number of the molecules in the critical cluster compared to results predicted by the present theory.

To illustrate the nature and consequences of Eqs. (12)–(13) in terms of the cluster size, we calculated the sizes of the critical clusters consisting of sulfuric acid and water, which are presented in Fig. 5. As may be seen from Fig. 5, the deviation between the classical IIN theory and the present study is about 15%. This difference may give several orders of magnitude in the nucleation rates because the nucleation rates are known to be very sensitive to the size of the critical cluster.

4. Conclusions

In this paper we derived the model of ion-induced nucleation of two-component polar vapours. It has been shown that the formation of small ion clusters is influenced by the vapour polarity and the dipole-charge interaction decreases the size of critical clusters formed. It has been shown that the actual size of small binary ion clusters may deviate significantly from the size predicted by classical Kelvin-Thomson theory, when the nucleating vapours are highly polar. The derived model can be considered as a generalized reformulation of the classical IIN theory that accounts for such microphysical properties as dipole moment and polarization of the nucleating vapours.

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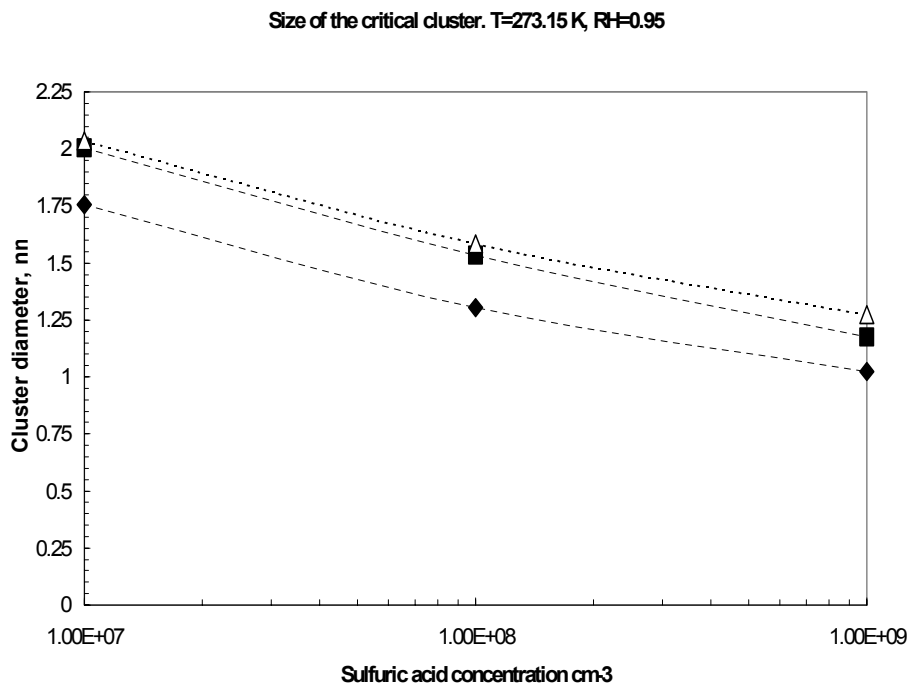© EGU 2003

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Size of the critical cluster. T=273.15 K, RH=0.95
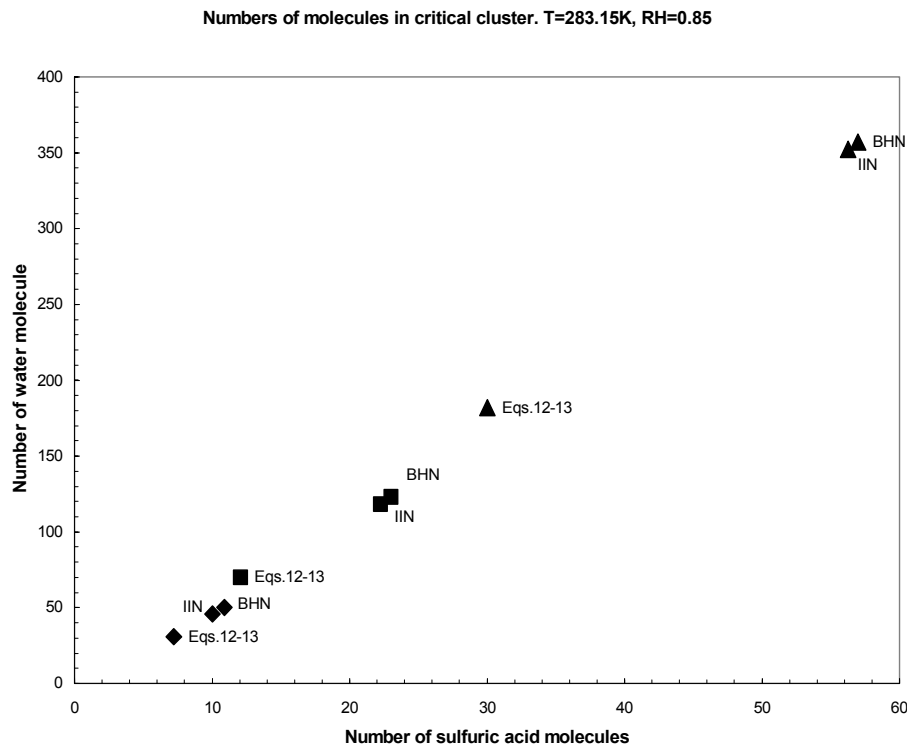

Fig. 1. Numbers of molecules in critical cluster as a function of temperature, relative humidity and sulfuric acid concentration. Triangles correspond to the sulfuric acid concentration of 10^7, squares to that of 10^8 and diamonds to that of $10^9 \, cm^{-3}$. T = 273.15 K, RH = 0.85.

Numbers of molecules in critical cluster. T=273 K, RH=0.95
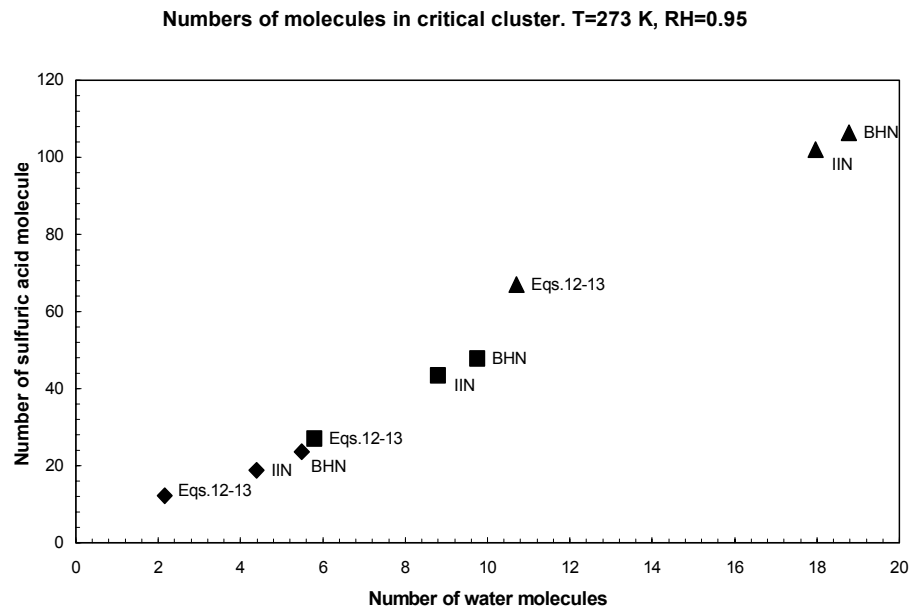
Fig. 2. Numbers of molecules in critical cluster as a function of temperature, relative humidity and sulfuric acid concentration. Triangles correspond to the sulfuric acid concentration of 10^7, squares to that of 10^8 and diamonds to that of $10^9 \, cm^{-3}$. $T = 273.15 \, K$, RH = 0.95.

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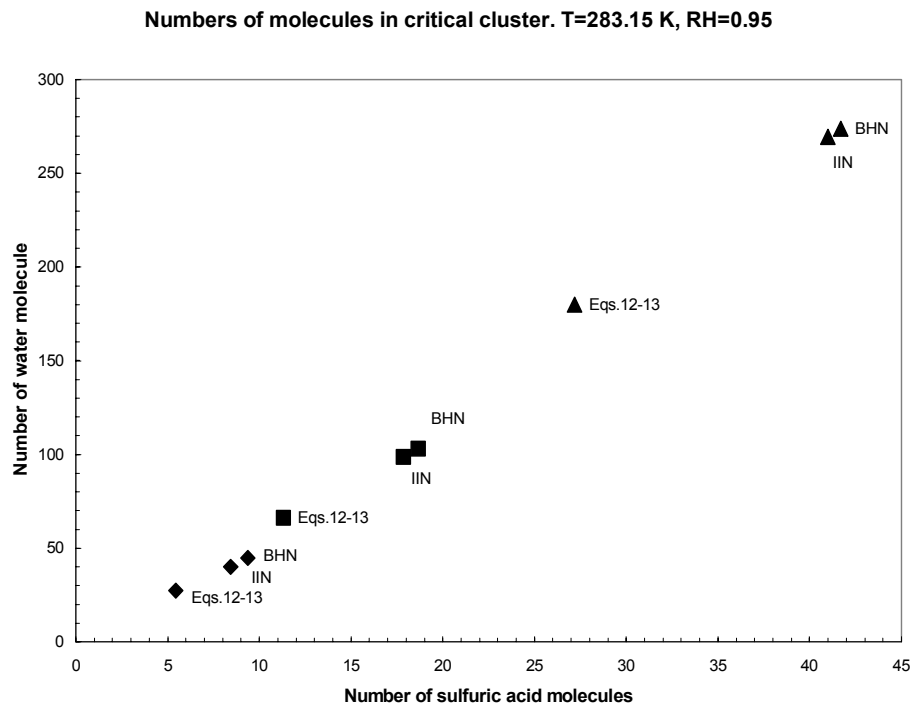Numbers of molecules in critical cluster. T=283.15K, RH=0.85

Fig. 3. Numbers of molecules in critical cluster as a function of temperature, relative humidity and sulfuric acid concentration. Triangles correspond to the sulfuric acid concentration of 10^7, squares to that of 10^8 and diamonds to that of 10^9 cm^{-3}. T = 283.15 K, RH = 0.85.

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Numbers of molecules in critical cluster. T=283.15 K, RH=0.95

Fig. 4. Numbers of molecules in critical cluster as a function of temperature, relative humidity and sulfuric acid concentration. Triangles correspond to the sulfuric acid concentration of 10^7, squares to that of 10^8 and diamonds to that of $10^9 \, \mathrm{cm}^{-3}$. $T = 283.15 \, \mathrm{K}$, RH = 0.95.

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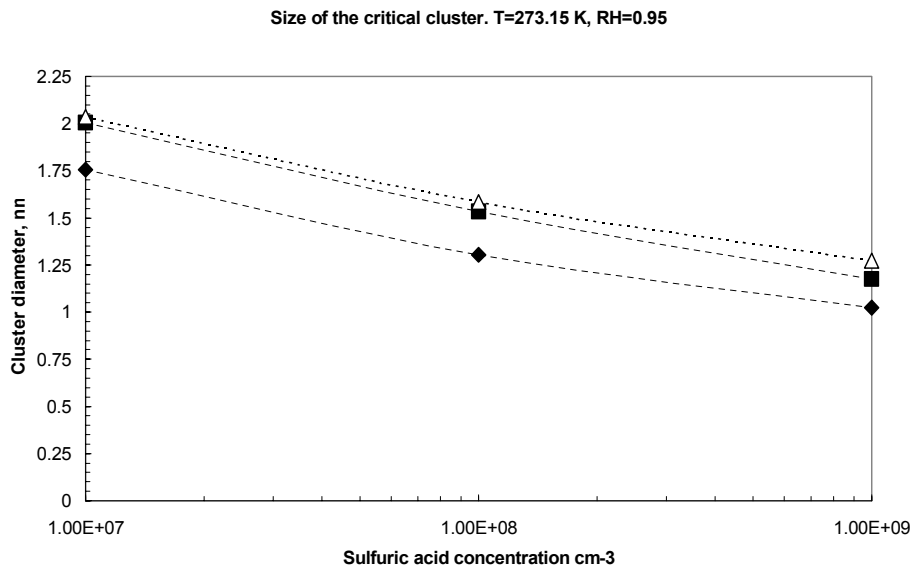Size of the critical cluster. T=273.15 K, RH=0.95

Fig. 5. Size of the critical cluster given by different models. Triangles correspond to BHN, squares to classical IIN and diamonds present the results of the present study. $T = 273.15\,\text{K}$, RH = 0.95.