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# Calculation of Composition Distribution of Ultrafine Ion-H<sub>2</sub>O-H<sub>2</sub>SO<sub>4</sub> Clusters Using a Modified Binary Ion-Nucleation Theory

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# Calculation of Composition Distribution of Ultrafine Ion-H<sub>2</sub>O-H<sub>2</sub>SO<sub>4</sub> Clusters Using a Modified Binary Ion-Nucleation Theory

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## SUMMARY

Thomson's ion-nucleation theory for binary mixtures has been modified to include the effects of curvature dependence of microscopic surface tension, of field-dependent nonlinear dielectric behavior of the nucleating mixture in the immediate vicinity of the ion, and of neutral clustering prior to ion-induced nucleation. The modified theory has been applied to calculate the composition distribution of ultrafine ion-H<sub>2</sub>O-H<sub>2</sub>SO<sub>4</sub> clusters for various combinations of relative humidity and relative acidity. Comparisons of the ion-cluster spectra predicted on the basis of the conventional Thomson theory and the modified theory reveal that a much broader spectrum is obtained using the latter theory, especially for higher values of relative humidity and relative acidity. For an increase in relative humidity and relative acidity, the tendency for the cluster spectrum is to spread towards larger groups containing larger numbers of water and sulfuric acid molecules in them. A lowering of the temperature also leads to a broadening of the ion-cluster spectrum and to an increase in the number of water and sulfuric acid molecules in the clusters. It thus appears that the formation of stable prenucleation ion-H<sub>2</sub>O-H<sub>2</sub>SO<sub>4</sub> clusters is enhanced by an increase in relative acidity, an increase in relative humidity, and a decrease in temperature. An important finding of this study is that even a trace of sulfuric acid at low temperatures enhances the probability of approaching the critical saddle-point condition for growth to larger molecular clusters.

## INTRODUCTION

Positive and negative ion clusters exist throughout the atmosphere (Mohnen 1971). Also, ionic processes play an important role in the upper atmosphere (Ferguson et al. 1979). Whenever sulfuric acid and water molecules exist in the atmosphere, an important mechanism for gas-to-particle conversion is believed to be via ion-induced nucleation. Hence, it is desirable to have a clear understanding of the theory governing this process. In this paper some of the shortcomings of the conventional theory are examined and several modifications to improve its applicability are proposed. Even though the study of ion nucleation in a binary mixture of sulfuric acid and water vapors is emphasized, the modifications are equally valid for binary nucleation without ions.

As pointed out in the literature (Burton and Briant 1977, Castleman et al. 1978, and Chan and Mohnen 1980), the conventional Thomson equation (Thomson and Thomson 1928) carries all the shortcomings of the classical droplet model. Several papers have been published recently dealing with some of these problems. Vogelsberger (1980) discussed the influence of curvature-dependent surface tension on the free energy of formation of microclusters. Liszi et al. (1981) developed an electric-field-dependent Kirkwood factor for nonlinear dielectric behavior of some liquids. Chan and Mohnen (1980) combined the effects of curvature-dependent surface tension and nonlinear dielectric behavior of liquids in their discussion of the nucleation of water on ions. Heist and Reiss (1974) demonstrated that sulfuric acid hydrates are important in the nucleation process involving water and sulfuric acid molecules. All these modifications are introduced into the theory and are used to study the gas-to-particle conversion process that leads to the formation of ultrafine background sulfate aerosols in the presence of ions. It is shown that the present calculations corroborate the findings of Castleman and Tang (1972), which show that small ion

clusters comprise a significant segment of the overall nucleation size spectrum. It is also shown that prenucleation ion clusters play an important role in nucleation processes.

#### SYMBOLS

E	electric field
F	cavity field
$\Delta G$	free energy of droplet formation
g	field-dependent Kirkwood factor
k	Boltzmann constant
L(x)	Langevin function, $\coth(x) - \frac{1}{x}$
N	number of molecules per unit volume
$N_{A,B}$	total number of molecules of component A or B in the system
$n_{A,B}$	number of molecules of component A (water) or B (sulfuric acid) in cluster
$P(n_A, n_B)$	probability of occurrence of the ion cluster containing $n_A$ molecules of component A and $n_B$ molecules of component B
$P_{A,B}$	equilibrium vapor pressure of component A or B
$P_A^0$	saturation vapor pressure of component A
$P_B^0$	saturation vapor pressure of component B
$P_{A,B}^{sol}$	equilibrium vapor pressure of component A or B over flat surface of solution
$P'_{A,B}$	partial pressure of component A or B after AB compound formation
Q	ionic charge on cluster
R.A.	relative acidity ( $S_B$ in eq. (18))
R.H.	relative humidity ( $S_A$ in eq. (18))
r	radius of droplet
$r_1$	ionic radius
T	absolute temperature
$\alpha_A$	water activity
$\alpha_B$	acid activity

$\beta$	$= \frac{3\mu}{2kT}$ (for $2\epsilon \gg \eta^2$ )
$\delta$	Tolman coefficient
$\epsilon$	dielectric constant of mixture
$\eta$	internal refractive index of liquid
$\mu$	field-dependent dipole moment, $\frac{n^2+2}{3} \mu_0 g^{1/2}$
$\mu_0$	dipole moment in absence of field
$\sigma$	surface tension of droplet
$\sigma_0$	surface tension of plane surface

#### THE MODIFIED BINARY ION-NUCLEATION THEORY FOR MIXTURE OF VAPORS

The conventional Thomson theory (Thomson and Thomson 1928) for a binary mixture of vapors states that the free energy of formation of a droplet  $\Delta G$  with  $n_A$  molecules of substance A and  $n_B$  molecules of substance B around an ion core with charge  $Q$  and radius  $r_1$  is given by the following equation:

$$\Delta G(n_A, n_B) = -n_A kT \ln \frac{P_A}{P_A^{sol}} - n_B kT \ln \frac{P_B}{P_B^{sol}} + 4\pi r^2 \sigma + \frac{Q^2}{2} \left(1 - \frac{1}{\epsilon}\right) \left(\frac{1}{r} - \frac{1}{r_1}\right) \quad (1)$$

where

$k$	Boltzmann constant
$T$	absolute temperature
$P_{A,B}$	equilibrium vapor pressure of component A or B
$P_{A,B}^{sol}$	equilibrium vapor pressure of component A or B over flat surface of solution
$r$	radius of droplet
$\sigma$	surface tension of droplet
$\epsilon$	dielectric constant of mixture

In this paper,  $n_A$  and  $n_B$  are used to denote the number of water and sulfuric acid molecules in the ion cluster, respectively.

A major criticism of Thomson's theory is that bulk values for the surface tension and dielectric constant are used. Feder et al. (1966) pointed out that a 15-percent change in the surface tension of a small droplet may affect the nucleation rate by a factor of  $10^{17}$ . Liszi et al. (1981) demonstrated that nonlinear dielectric

behavior is important in the study of ions in electrolytic solutions. Besides these shortcomings, Thomson's theory (eq. (1)), as applied to droplets containing water and sulfuric acid, does not take into account the formation of sulfuric acid hydrates. Corrections for all these defects are discussed in the sections that follow.

### Curvature-Dependent Surface-Tension Correction

The variation of bulk surface tension  $\sigma_0$  of the solution of water and sulfuric acid with composition can be obtained from the published data of Sabinina and Terpugov (1935). A discussion of the influence of curvature effect on the free energy of formation of microclusters can be found in some recent papers (Hamill et al. 1974, and Vogelsberger 1980). The relationship between the surface tension and the radius of curvature of a liquid surface is given by the generalized Tolman differential equation (Nonnenmacher 1977). For a convex or concave surface,<sup>1</sup>

$$\delta \left[ r^2 \frac{d^2 \sigma(r)}{dr^2} \right] + r(2\delta \pm r) \frac{d\sigma(r)}{dr} - 2\delta\sigma(r) = 0 \quad (2)$$

where  $\sigma(r)$  is the curvature-dependent surface tension and  $\delta$  is the Tolman coefficient. The complete solution of this equation (Nonnenmacher 1977) is

$$\sigma(r) = c_1 \left( 1 \mp 2\delta/r + 2\delta^2/r^2 \right) + (c_2/r^2) \exp(\mp r/\delta) \quad (3)$$

The boundary condition

$$\lim_{r \rightarrow \infty} \sigma(r) = \sigma_0$$

leads to  $c_1 = \sigma_0$  where  $\sigma_0$  is the surface tension of the plane surface. If  $c_2$  is assumed to have the same values on both convex and concave surfaces, then

$$c_2 = 0$$

and

$$\sigma(r) = \sigma_0 \left( 1 - \frac{2\delta}{r} + 2\delta^2/r^2 \right) \quad (4)$$

---

<sup>1</sup>The upper signs in equations (2) and (3) refer to a convex surface, and the lower signs refer to a concave surface.



If we assume that the surface energy of a spherical droplet  $4\pi r^2\sigma$  approaches zero as  $r$  approaches zero, then equation (3) takes the form

$$\sigma(r) = \sigma_0(1 - 2\delta/r + 2\delta^2/r^2) - 2\delta^2\sigma_0/r^2 \exp(-r/\delta) \quad (5)$$

On the other hand, if we define a surface of tension (Nonnenmacher 1977) by setting

$\frac{d\sigma}{dr} = 0$ , equation (3) then reduces to

$$\sigma(r) = \sigma_0 \left(1 + \frac{2\delta}{r}\right)^{-1} \quad (6)$$

which is identical to Tolman's result (Tolman 1949). This expression shows that  $\sigma(r)$  decreases with decreasing radius. Vogelsberger (1980) suggested 0.92 Å as the value of  $\delta$ .

#### Field-Dependent Nonlinear Behavior of Dielectric Properties of Liquids

For high electric fields such as those in the immediate neighborhood of an ion, the linear correlation between dielectric polarization and electric field breaks down. This phenomenon is commonly referred to as the dielectric saturation effect. A modified form of a recent theory developed by Liszi et al. (1981), which describes the dielectric behavior of liquids in the vicinity of ions in electrolytic solutions, is adopted here.

According to the Booth-Onsager theory (Booth 1951), the relative permittivity  $\epsilon$  depends on the electric field as follows:

$$\epsilon = \eta^2 + \frac{4\pi N\mu}{E} L\left(\frac{\mu F}{kT}\right) \quad (7)$$

where

- F cavity field, given by  $\frac{3\epsilon}{2\epsilon + \eta^2} E$
- $\eta$  internal refractive index of liquid
- k Boltzmann constant
- T temperature
- $\mu$  actual dipole moment
- E electric field

N number of molecules per unit volume

L(x) Langevin function,  $\coth(x) - \frac{1}{x}$

For liquids in which the molecules are in nonrandom orientation because of hydrogen bonding or some other structural effects, Liszi et al. (1981) proposed a field-dependent Kirkwood factor correction term for  $\mu$ . If  $\epsilon_0$  is the dielectric constant at a large distance from the ion source, i.e., for a weak field, the effective dielectric constant  $\epsilon$  can be put into the form (Chan and Mohnen 1980)

$$\epsilon = \eta^2 + (\epsilon_0 - \eta^2) \frac{3}{\beta E} \left[ \frac{1}{\tanh(\beta E)} - \frac{1}{\beta E} \right] \quad (8)$$

where

$$E = \frac{Q}{\epsilon r^2} \quad (9)$$

and

$$\beta = \frac{3\mu}{2kT} \quad (\text{for } 2\epsilon \gg \eta^2) \quad (10)$$

where

$$\mu = \frac{\eta^2 + 2}{3} \mu_0 g^{1/2} \quad (11)$$

Here,  $\mu_0$  is the dipole moment in the absence of the field, and  $g$  is the field-dependent Kirkwood factor defined as follows:

$$g = g_0 + g_1 E^2 + g_2 E^4 + g_3 E^6 + \dots \quad (12a)$$

If higher terms in  $E$  are neglected, then

$$g \approx 1 + \frac{g_0 - 1}{1 - [g_1 E^2 / (g_0 - 1)]} \quad (12b)$$

The values of  $g_0$  and  $g_1$  for water given by Liszi et al. (1981) are as follows:  $g_0 = 2.8$  and  $g_1 = -0.56 \times 10^{-8}$  (when  $E$  is expressed in esu). Internal refractive indices of sulfuric acid and water solutions of varying strengths have been reported in the literature (Mellor 1930) and are given below:

Refractive index	Weight percent H <sub>2</sub> SO <sub>4</sub>					
	0	20	40	60	80	100
$\eta$	1.336	1.3578	1.3817	1.4065	1.4308	1.4377

The value of  $\epsilon_0$  for the solution is found by using the additivity of dielectric constant of components upon a volume-fraction basis.

#### Effect of Sulfuric Acid Hydrates on the Free Energy of Cluster Formation

Heist and Reiss (1974) suggested that sulfuric acid hydrates are important in the H<sub>2</sub>O-H<sub>2</sub>SO<sub>4</sub> nucleation process. For a concentration of water molecules much higher than that of sulfuric acid molecules, we can assume that the formation of H<sub>2</sub>SO<sub>4</sub> hydrates does not appreciably change the concentration of H<sub>2</sub>O molecules and that the sum of H<sub>2</sub>O molecules and H<sub>2</sub>SO<sub>4</sub> hydrates equals the initial number of H<sub>2</sub>SO<sub>4</sub> molecules. If the actual partial pressure of sulfuric acid and water vapor in a system having hydrates is given by  $p'_B$  and  $p'_A$ , then following the procedure given by Heist and Reiss (1974), the actual free energy of formation of neutral (H<sub>2</sub>O)<sub>n<sub>A</sub></sub> · (H<sub>2</sub>SO<sub>4</sub>)<sub>n<sub>B</sub></sub> hydrates is

$$\Delta G(n_A, n_B) = -n_A kT \ln \frac{p'_A}{p_A} - n_B kT \ln \frac{p'_B}{p_B} + 4\pi r^2 \sigma \quad (13)$$

When the number of water molecules is much greater than the number of sulfuric acid hydrates, the partial vapor pressure of water can be assumed to remain essentially unchanged; that is,  $p'_A = p_A$ . Thus, equation (13) takes the form

$$\begin{aligned} \Delta G &= -n_A kT \ln \frac{p_A}{p_A} - n_B kT \ln \frac{p_B}{p_B} - n_B kT \ln \frac{p'_B}{p_B} + 4\pi r^2 \sigma \\ &= \Delta G_0(n_A, n_B) - n_B kT \ln \frac{p'_B}{p_B} \end{aligned} \quad (14)$$

where  $\Delta G_0$  represents the free energy without the presence of hydrates.

Suzuki and Mohnen (1981) estimated that even though higher-order sulfuric acid hydrates are present, the monomer hydrates dominate. Hence,

$$\sum_{n_A} \sum_{n_B} N(n_A, n_B) = \sum_{n_A} \sum_{n_B} N_A \left( \frac{p'_B}{p_B} \right)^{n_B} \exp \left[ - \frac{\Delta G_0(n_A, n_B)}{kT} \right] = N_B \left( 1 - \frac{p'_B}{p_B} \right) \quad (15)$$

where  $N_A$  and  $N_B$  are the total number of molecules A and B in the system, and  $N(n_A, n_B)$  is the number of clusters containing  $n_A$  and  $n_B$  molecules. The value of  $p'_B/p_B$  is obtained by numerical solution of equation (15).

### Modified Equation

In the preceding sections, various improvements that can be made in the conventional Thomson equation have been discussed. Incorporating all these corrections, the equation for free energy of formation  $\Delta G$  can be written as follows:

$$\begin{aligned} \Delta G(n_A, n_B) = & -n_A kT \ln \frac{p_A}{p_A^{\text{sol}}} - n_B kT \ln \frac{p_B}{p_B^{\text{sol}}} + 4\pi r^2 \sigma \\ & - n_B kT \ln \frac{p'_B}{p_B} + \frac{Q^2}{2} \left( \frac{1}{r} - \frac{1}{r_1} \right) + \frac{Q^2}{2} \int_{r_1}^r \frac{dr}{\epsilon r^2} \end{aligned} \quad (16)$$

The variation of  $\sigma$  with the radius of curvature of the droplet is given by equation (6). The variation of  $\epsilon$  with composition is given by equations (8)

through (12). The last term in equation (16) replaces the  $-Q^2/2\epsilon \left( \frac{1}{r} - \frac{1}{r_1} \right)$  term in equation (1). The value of  $p'_B/p_B$  is obtained by solving equation (15) numerically, assuming that the formation of ion clusters and  $\text{H}_2\text{SO}_4$  hydrates does not noticeably change the values of participating  $\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4$  molecular concentrations in the reaction chamber. The saturated sulfuric acid vapor pressure over solutions of varying composition and temperature is given by Ayers et al. (1980) as

$$\ln p_B^{\text{sol}} = - \frac{10156 \pm 175}{T} + (16.259 \pm 0.437) + \frac{\mu - \mu_0}{8.3143T} \quad (17)$$

where  $p_B^{\text{sol}}$  is in atm and the composition-dependent term  $\mu - \mu_0$  is found in the tables of Giaouque et al. (1960). Values for  $p_A^{\text{sol}}$  can also be obtained from these tables. Equation (17) was derived by generalization of the results based on experimental data. The values of vapor pressures obtained using this equation are about an order of magnitude lower than the commonly used values given by Gmitro and Vermeulen (1964). Similar results were obtained by Roedel (1979). By using the new more reliable acid vapor-pressure values, another source of error is eliminated. This is because the calculated free energy of cluster formation is strongly dependent upon the value of sulfuric acid vapor pressure chosen as input to the computations. Application of the modified theory to the calculation of spectral distribution of ultrafine ion- $\text{H}_2\text{O}$ - $\text{H}_2\text{SO}_4$  clusters under various conditions of relative acidity, relative humidity, and temperature is discussed in the following section.

CALCULATION OF COMPOSITION DISTRIBUTION OF

ULTRAFINE ION-H<sub>2</sub>O-H<sub>2</sub>SO<sub>4</sub> CLUSTERS

Sometimes it is more convenient to express the equation for the free energy of formation of ion-H<sub>2</sub>O-H<sub>2</sub>SO<sub>4</sub> clusters in terms of the relative humidity  $S_A$ , the water activity  $\alpha_A$ , the relative acidity  $S_B$ , and the acid activity  $\alpha_B$ , defined as

$$S_A = p_A / p_A^{\circ}$$

$$\alpha_A = p_A^{\text{sol}} / p_A^{\circ}$$

$$S_B = \frac{p_B}{p_B^{\circ}}$$

and

$$\alpha_B = p_B^{\text{sol}} / p_B^{\circ}$$

where

$p_A^{\circ}$  saturation vapor pressure of pure water

$p_B^{\circ}$  saturation vapor pressure of pure sulfuric acid

Substituting these terms into equation (16) yields

$$\begin{aligned} \Delta G(n_A, n_B) = & -n_A kT \ln \frac{S_A}{\alpha_A} - n_B kT \ln \frac{S_B}{\alpha_B} + 4\pi r^2 \sigma \\ & - n_B kT \ln \frac{p_B'}{p_B} + \frac{Q^2}{2} \left( \frac{1}{r} - \frac{1}{r_1} \right) + \frac{Q^2}{2} \int_{r_1}^r \frac{1}{\epsilon r^2} dr \end{aligned} \quad (18)$$

For given values of  $S_A$ ,  $S_B$ , and  $T$ ,  $\Delta G(n_A, n_B)$  can be calculated for different values of  $n_A$  and  $n_B$ ; hence, the size distribution of the ion clusters can be computed. The probability of existence given as a percentage in the ion-cluster spectrum  $P(n_A, n_B)$  is

$$P(n_A, n_B) = \frac{100 \exp[-\Delta G(n_A, n_B)(kT)^{-1}]}{\sum_{n_A} \sum_{n_B} \exp[-\Delta G(n_A, n_B)(kT)^{-1}]} \quad (19)$$

For actual calculations of  $P(n_A, n_B)$ , the following values of various parameters in equation (19) have been used:

$Q$  charge on  $H^+ \cdot H_2O$  ion,  $4.8 \times 10^{-10}$  esu

$r_1$  radius of  $H^+ \cdot H_2O$  ion, 1.38 Å

The values for  $\sigma_o(T)$  and  $\epsilon_o(T)$  are taken from the International Critical Tables (NRC 1929) for appropriate mixtures of  $H_2O$  and  $H_2SO_4$ .

Typical comparisons of the predicted spectral ion-cluster distributions between the Thomson model and the modified model illustrate the effects of the modifications made. The clusters listed in tables 1 through 3 fall into the following groups (the first number within the parentheses represents the number of  $H_2SO_4$  molecules, the second number represents the number of  $H_2O$  molecules, and the third number represents the ionic charge on the clusters):

Group 1	(1, x, 1)	Group 4	(4, x, 1)
Group 2	(2, x, 1)	Group 5	(5, x, 1)
Group 3	(3, x, 1)	Group 6	(6, x, 1)

The ion is taken to be  $H^+ \cdot H_2O$ , and its number in the cluster is always 1.

The tables show that the clusters predicted by the Thomson theory generally fall into smaller groups and are not as widely spread among the groups as the modified theory predicts. In the group representation, the group number and the number of sulfuric acid molecules increase together, and the number of water molecules in the microcluster is represented by  $x$ . Examination of tables 1 through 3 reveals that for higher relative acidity or greater relative humidity, there is more spreading out of the ion-cluster spectrum towards higher groups for the modified theory, but the spectrum derived from the Thomson theory is still characterized by relatively fewer and smaller groups. Thus the modified theory provides a much broader ion-cluster spectrum, especially when the relative acidity (R.A.) and/or relative humidity (R.H.) are relatively high. These trends are consistent with the experimental results of Singh et al. (1982).

With more features relevant to small ion clusters, it is no surprise that the modified theory predicts a larger (broader) ion-cluster spectrum. The modified theory has been applied for further study of the influence of relative acidity, relative humidity, and temperature on the microcluster distribution spectra.

The calculated percentage of ion clusters containing  $n_A$  and  $n_B$  molecules for R.H. = 0.1 and R.A. =  $1 \times 10^{-6}$ ,  $1 \times 10^{-5}$ ,  $1 \times 10^{-4}$ , and  $1 \times 10^{-3}$  at  $T = 27^\circ C$  is presented in table 4. Spreading out into higher groups with higher values of  $x$  is observed when the acidity is increased. A similar pattern persists when the relative humidity increases, but spreading towards a higher number of water molecules in

the same group is more significant than spreading towards higher groups. The variation of distribution spectrum with increases in R.H. is presented in table 5. For an increase in both R.A. and R.H., the tendency is to spread over higher groups and towards higher values of  $x$  in the same group. At the same time, the mean intensity for the distribution decreases as the mean radius of the ion clusters increases; that is, the chance of the dominance of a particular sector in the distribution diminishes. This feature leads to a more gentle sloping from the valley-stable condition for prenucleation ion clusters along the mountain pass towards the critical saddle-point condition for growth to larger clusters. If the slope of the pass becomes nearly flat, the stage is set for nucleation growth.

Distribution diagrams such as figures 1 through 3 are helpful for visualizing the effect of changes in various variables on the ion-cluster spectra. As shown in figures 1 and 2, a lowering of temperature helps to broaden the spectrum for the same R.A. and R.H. values. Further examination reveals that the effect of spreading towards higher groups is accompanied by spreading towards higher  $x$  values also. Figure 3 shows that even a trace of  $H_2SO_4$  (R.A. =  $1 \times 10^{-6}$ ) can lead to formation of larger clusters at low temperatures.

#### CONCLUDING REMARKS

A modified ion-nucleation theory for binary mixtures has been developed and applied to mixtures of sulfuric acid and water vapor. Curvature-dependent microscopic surface tension is used. Field-dependent, nonlinear dielectric behavior of the solution of water and sulfuric acid in the immediate neighborhood of an ion is considered. Also the effect of formation of sulfuric acid hydrates is taken into account. The radius dependence of the surface tension and the nonlinear dielectric behavior of the solution of water and sulfuric acid are more effective in producing a cluster spectrum change than the effect of sulfuric acid hydrate formation. Typical comparisons of the predicted ion-cluster spectra between the modified and Thomson theory reveal that a much broader cluster spectrum is obtained using the modified theory, especially for higher values of relative acidity (R.A.) and/or relative humidity (R.H.). For an increase in R.A. and/or R.H., the tendency is for the cluster spectrum to spread towards higher groups with larger numbers of sulfuric acid and water molecules in them. Whether the shift is towards higher groups or larger numbers of water molecules depends on the relative rates of increase of R.A. and R.H. A lowering of temperature leads to a broadening of the ion-cluster spectrum and to an increase in the number of sulfuric acid and water molecules in the clusters. These trends are consistent with the recently reported experimental results.

A broadening of the ion-cluster spectrum is usually accompanied by a lowering as well as a more even distribution of the ion-cluster intensity. Also, the mean radius of the ion clusters present in the spectrum increases. Thus, the formation of stable prenucleation ion- $H_2O$ - $H_2SO_4$  clusters is enhanced by an increase in R.A., an increase in R.H., and a decrease in temperature. An important result of this study is that even a trace of sulfuric acid (R.A. as low as  $1 \times 10^{-6}$ ) at low temperatures enhances the probability of approaching the critical saddle-point condition for growth to larger molecular clusters.

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## REFERENCES

- Ayers, G. P.; Gillett, R. W.; and Gras, J. L. 1980: On the Vapor Pressure of Sulfuric Acid. *Geophys. Res. Lett.*, vol. 7, no. 6, pp. 433-436.
- Booth, F. 1951: The Dielectric Constant of Water and the Saturation Effect. *J. Chem. Phys.*, vol. 19, no. 4, pp. 391-394. (Errata, vol. 19, no. 10, pp. 1327-1328.)
- Burton, J. J.; and Briant, C. L. 1977: Atomistic Models of Microclusters: Implications for Nucleation Theory. *Adv. Colloid & Interface Sci.*, vol. 7, pp. 131-203.
- Castleman, A. W., Jr.; Holland, Paul M.; and Keesee, Robert G. 1978: The Properties of Ion Clusters and Their Relationship to Heteromolecular Nucleation. *J. Chem. Phys.*, vol. 68, no. 4, pp. 1760-1767.
- Castleman, A. W., Jr.; and Tang, I. N. 1972: Role of Small Clusters in Nucleation About Ions. *J. Chem. Phys.*, vol. 57, no. 9, pp. 3629-3638.
- Chan, Lo Yin; and Mohnen, V. A. 1980: Ion Nucleation Theory. *J. Atmos. Sci.*, vol. 37, no. 10, pp. 2323-2331.
- Feder, J.; Russell, K. C.; Lothe, J.; and Pound, G. M. 1966: Homogeneous Nucleation and Growth of Droplets in Vapors. *Adv. Phys.*, vol. 15, no. 57, pp. 111-178.
- Ferguson, E. E.; Fehsenfeld, F. C.; and Albritton, D. L. 1979: Chapter 2 - Ion Chemistry of the Earth's Atmosphere. *Gas Phase Ion Chemistry, Volume 1*, Michael T. Bowers, ed., Academic Press, Inc., pp. 45-82.
- Giauque, W. F.; Hornung, E. W.; Kunzler, J. E.; and Rubin, T. R. 1960: The Thermodynamic Properties of Aqueous Sulfuric Acid Solutions and Hydrates From 15 to 300°K. *J. American Chem. Soc.*, vol. 82, no. 1, pp. 62-70.
- Gmitro, John Irving; and Vermeulen, Theodore 1964: Vapor-Liquid Equilibria for Aqueous Sulfuric Acid. *A.I.Ch.E. J.*, vol. 10, no. 5, pp. 740-746.
- Hamill, P.; Stauffer, D.; and Kiang, C. S. 1974: Nucleation Theory: Fisher's Droplet Picture and Microscopic Surface Tension. *Chem. Phys. Lett.*, vol. 28, no. 2, pp. 209-212.
- Heist, R. H.; and Reiss, H. 1974: Hydrates in Supersaturated Binary Sulfuric Acid-Water Vapor. *J. Chem. Phys.*, vol. 61, no. 2, pp. 573-581.
- Liszi, J.; Mészáros, L.; and Ruff, I. 1981: The Field Dependence of the Kirkwood Factor and the Nonlinear Dielectric Behavior of Some Liquids. *J. Chem. Phys.*, vol. 74, no. 12, pp. 6896-6901.
- Mellor, J. W. 1930: A Comprehensive Treatise on Inorganic and Theoretical Chemistry - Volume X. John Wiley & Sons, Inc., p. 409.



- Mohnen, Volker A. 1971: Discussion of the Formation of Major Positive and Negative Ions Up to the 50 km Level. Mesospheric Models and Related Experiments, G. Fiocco, ed., D. Reidel Pub. Co. (Dordrecht, Holland), pp. 210-219.
- National Research Council 1929: International Critical Tables. Vol. III, McGraw-Hill Book Co., Inc.
- Nonnenmacher, Theo F. 1977: Size Effect on Surface Tension of Small Droplets. Chem. Phys. Lett., vol. 47, no. 3, pp. 507-508.
- Roedel, Walter 1979: Measurement of Sulfuric Acid Saturation Vapor Pressure; Implications for Aerosol Formation by Heteromolecular Nucleation. J. Aerosol Sci., vol. 10, no. 4, pp. 375-386.
- Sabinina, L.; and Terpugov, L. 1935: The Surface Tension of the System Sulfuric Acid-Water. Z. Phys. Chem. (Neue Folge), vol. A173, pp. 237-241.
- Singh, J. J.; Smith, A. C.; and Yue, G. K. 1982: Experimental Studies of the Ion-Induced Binary Nucleation. J. Aerosol Sci., vol. 13, no. 4.
- Suzuki, Kunihiro; and Mohnen, Volker A. 1981: Binary Homogeneous Nucleation Theory by Cluster-Cluster Interaction With Application to the H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O System. J. Aerosol Sci., vol. 12, no. 1, pp. 61-73.
- Thomson, J. J.; and Thomson, G. P. 1928: Conduction of Electricity Through Gases. Volume I - General Properties of Ions Ionisation by Heat and Light, Third ed. Cambridge Univ. Press.
- Tolman, Richard C. 1949: The Effect of Droplet Size on Surface Tension. J. Chem. Phys., vol. 17, no. 3, pp. 333-337.
- Vogelsberger, Wolfram 1980: Influence of Curvature-Dependent Surface Tension on the Free Energy of Formation of Microclusters. Chem. Phys. Lett., vol. 74, no. 1, pp. 143-146.

TABLE 1.- COMPARISON OF CALCULATED PERCENTAGES OF ION CLUSTERS CONTAINING

 $n_A$  AND  $n_B$  MOLECULES USING THOMSON THEORY AND MODIFIED THEORYFOR  $R.A. = 1 \times 10^{-6}$ ,  $R.H. = 0.1$ , AND  $T = 27^\circ C$ 

[ Only ion-cluster intensities greater than 1 percent  
in the spectrum are listed ]

Theory	$P(n_B, n_A)$ for $n_B, n_A$ values of -								$\sum_{n_A} P(n_B, n_A)$ (1,x)
	1,2	1,3	1,4	1,5	1,6	1,7	1,8	1,9	
Thomson theory		2.5%	19.7%	33.7%	22.2%	8.1%	1.8%		88.0%
Modified theory			5.0%	17.1%	20.7%	12.6%	4.5%	1.1%	61.0%
	2,2	2,3	2,4	2,5	2,6	2,7	2,8	2,9	(2,x)
Thomson theory				2.9%	4.1%	2.4%	1.0%		10.4%
Modified theory				4.4%	11.2%	11.3%	6.9%	2.8%	36.6%

TABLE 2.- COMPARISON OF CALCULATED PERCENTAGES OF ION CLUSTERS CONTAINING

$n_A$  AND  $n_B$  MOLECULES FOR THOMSON THEORY AND MODIFIED THEORY FOR

R.A. =  $1 \times 10^{-3}$ , R.H. = 0.1, AND T = 27°C

[Only ion-cluster intensities greater than 1 percent  
in the spectrum are listed]

Theory	$P(n_B, n_A)$ for $n_B, n_A$ values of -														$\sum_{n_A} P(n_B, n_A)$
	2,2	2,3	2,4	2,5	2,6	2,7	2,8	2,9	2,10	2,11	2,12	2,13	2,14	2,15	
Thomson theory			2.6%	7.9%	11.0%	6.5%	2.4%								30.4%
Modified theory					1.0%	1.2%									2.3%
	3,2	3,3	3,4	3,5	3,6	3,7	3,8	3,9	3,10	3,11	3,12	3,13	3,14	3,15	(3,x)
Thomson theory				3.4%	10.2%	14.2%	12.1%	7.5%	2.4%						49.8%
Modified theory					2.4%	5.8%	8.2%	8.1%	3.9%	1.6%					30.0%
	4,2	4,3	4,4	4,5	4,6	4,7	4,8	4,9	4,10	4,11	4,12	4,13	4,14	4,15	(4,x)
Thomson theory							1.9%	3.4%	3.6%	2.8%	1.7%				13.4%
Modified theory							1.5%	4.5%	7.8%	9.1%	8.3%	4.6%	1.8%		37.6%
	5,2	5,3	5,4	5,5	5,6	5,7	5,8	5,9	5,10	5,11	5,12	5,13	5,14	5,15	(5,x)
Thomson theory															<1%
Modified theory								1.2%	2.6%	3.6%	4.0%	3.3%	2.3%	1.0%	18.0%
	6,2	6,3	6,4	6,5	6,6	6,7	6,8	6,9	6,10	6,11	6,12	6,13	6,14	6,15	(6,x)
Thomson theory															<1%
Modified theory												1.1%	1.1%		2.2%

TABLE 3.- COMPARISON OF CALCULATED PERCENTAGES OF ION CLUSTERS CONTAINING

 $n_A$  AND  $n_B$  MOLECULES FOR THOMSON THEORY AND MODIFIED THEORY FORR.A. =  $1 \times 10^{-6}$ , R.H. = 0.50, AND T = 27°C

[ Only ion-cluster intensities greater than 1 percent in the  
spectrum are listed ]

Theory	P( $n_B, n_A$ ) for $n_B, n_A$ values of -															$\sum_{n_A} P(n_B, n_A)$ (1,x)
	1,2	1,3	1,4	1,5	1,6	1,7	1,8	1,9	1,10	1,11	1,12	1,13	1,14	1,15	1,16	
Thomson theory				2.1%	6.9%	12.6%	13.8%	10.8%	6.9%	3.5%	1.6%					58.2%
Modified theory						1.6%	2.8%	3.5%	3.3%	2.5%	1.6%					15.3%
	2,2	2,3	2,4	2,5	2,6	2,7	2,8	2,9	2,10	2,11	2,12	2,13	2,14	2,15	2,16	(2,x)
Thomson theory					1.3%	3.7%	6.7%	8.5%	7.1%	5.6%	3.3%	1.8%				38.0%
Modified theory						1.4%	4.4%	8.8%	11.1%	13.1%	10.9%	8.6%	5.1%	2.9%	1.5%	67.8%
	3,2	3,3	3,4	3,5	3,6	3,7	3,8	3,9	3,10	3,11	3,12	3,13	3,14	3,15	3,16	(3,x)
Thomson theory																
Modified theory										1.3%	1.7%	2.2%	2.0%	1.7%	1.3%	10.2%

TABLE 4.- VARIATION OF ION-CLUSTER SPECTRUM WITH CHANGE IN RELATIVE ACIDITY

(MODIFIED THEORY) FOR R.H. = 0.1, R.A. =  $1 \times 10^{-6}$ ,  $1 \times 10^{-5}$ ,

$1 \times 10^{-4}$ ,  $1 \times 10^{-3}$ , AND T = 27°C

[Only ion-cluster intensities greater than 1 percent in the spectrum are listed]

R.A.	P(n <sub>B</sub> ,n <sub>A</sub> ) for n <sub>B</sub> ,n <sub>A</sub> values of -													∑ <sub>n<sub>A</sub></sub> P(n <sub>B</sub> ,n <sub>A</sub> )
	1,2	1,3	1,4	1,5	1,6	1,7	1,8	1,9	1,10	1,11	1,12	1,13	1,14	(1,x)
1(-6) 1(-5) 1(-4) 1(-3)			5.0%	17.1%	20.7%	12.6%	4.5%	1.1%						61.0% 11.7% <1% <1%
	2,2	2,3	2,4	2,5	2,6	2,7	2,8	2,9	2,10	2,11	2,12	2,13	2,14	(2,x)
1(-6) 1(-5) 1(-4) 1(-3)				4.4%	11.2%	11.3%	6.9%	2.8%						36.6% 80.2% 50.1% 2.3%
	3,2	3,3	3,4	3,5	3,6	3,7	3,8	3,9	3,10	3,11	3,12	3,13	3,14	(3,x)
1(-6) 1(-5) 1(-4) 1(-3)						1.2%	1.7%	1.6%						<1% 4.5% 39.9% 30.0%
	4,2	4,3	4,4	4,5	4,6	4,7	4,8	4,9	4,10	4,11	4,12	4,13	4,14	(4,x)
1(-6) 1(-5) 1(-4) 1(-3)														<1% <1% 3.3% 37.6%
	5,2	5,3	5,4	5,5	5,6	5,7	5,8	5,9	5,10	5,11	5,12	5,13	5,14	(5,x)
1(-6) 1(-5) 1(-4) 1(-3)														<1% <1% <1% 17.0%
	6,2	6,3	6,4	6,5	6,6	6,7	6,8	6,9	6,10	6,11	6,12	6,13	6,14	(6,x)
1(-6) 1(-5) 1(-4) 1(-3)												1.0%	1.1%	<1% <1% <1% 2.1%

TABLE 5.- VARIATION OF ION-CLUSTER SPECTRUM WITH INCREASE IN RELATIVE HUMIDITY (MODIFIED THEORY)

FOR R.A. =  $1 \times 10^{-5}$ , R.H. = 0.01, 0.10, 0.50, AND T = 27°C

[ Only ion-cluster intensities greater than 1 percent  
in the spectrum are listed ]

R.H.	P(n <sub>B</sub> , n <sub>A</sub> ) for n <sub>B</sub> , n <sub>A</sub> values of -																				$\sum_{n_A} P(n_B, n_A)$
	1,2	1,3	1,4	1,5	1,6	1,7	1,8	1,9	1,10	1,11	1,12	1,13	1,14	1,15	1,16	1,17	1,18	1,19	1,20	1,21	
0.01 .10 .50		9.7%	19.4% 1.1%	7.3% 3.6%	4.4%	2.7%															36.4% 11.8% <1%
	2,2	2,3	2,4	2,5	2,6	2,7	2,8	2,9	2,10	2,11	2,12	2,13	2,14	2,15	2,16	2,17	2,18	2,19	2,20	2,21	(2,x)
0.01 .10 .50		9.6%	26.6% 1.4%	18.9% 9.2%	5.3% 23.6%	23.9%	14.6% 1.6%	5.9% 3.2%	1.5% 4.1%	4.8%	4.0%	3.2%	1.9%	1.1%							60.4% 80.1% 23.9%
	3,2	3,3	3,4	3,5	3,6	3,7	3,8	3,9	3,10	3,11	3,12	3,13	3,14	3,15	3,16	3,17	3,18	3,19	3,20	3,21	(3,x)
0.01 .10 .50								1.2% 1.0%	1.7% 2.2%	1.6% 4.7%	6.2%	8.2%	7.4%	6.3%	4.8%	3.1%	1.8%	1.1%			<1% 4.5% 46.8%
	4,2	4,3	4,4	4,5	4,6	4,7	4,8	4,9	4,10	4,11	4,12	4,13	4,14	4,15	4,16	4,17	4,18	4,19	4,20	4,21	(4,x)
0.01 .10 .50												1.3%	2.3%	2.9%	3.2%	3.5%	2.9%	2.0%	1.6%	1.1%	<1% <1% 20.8%

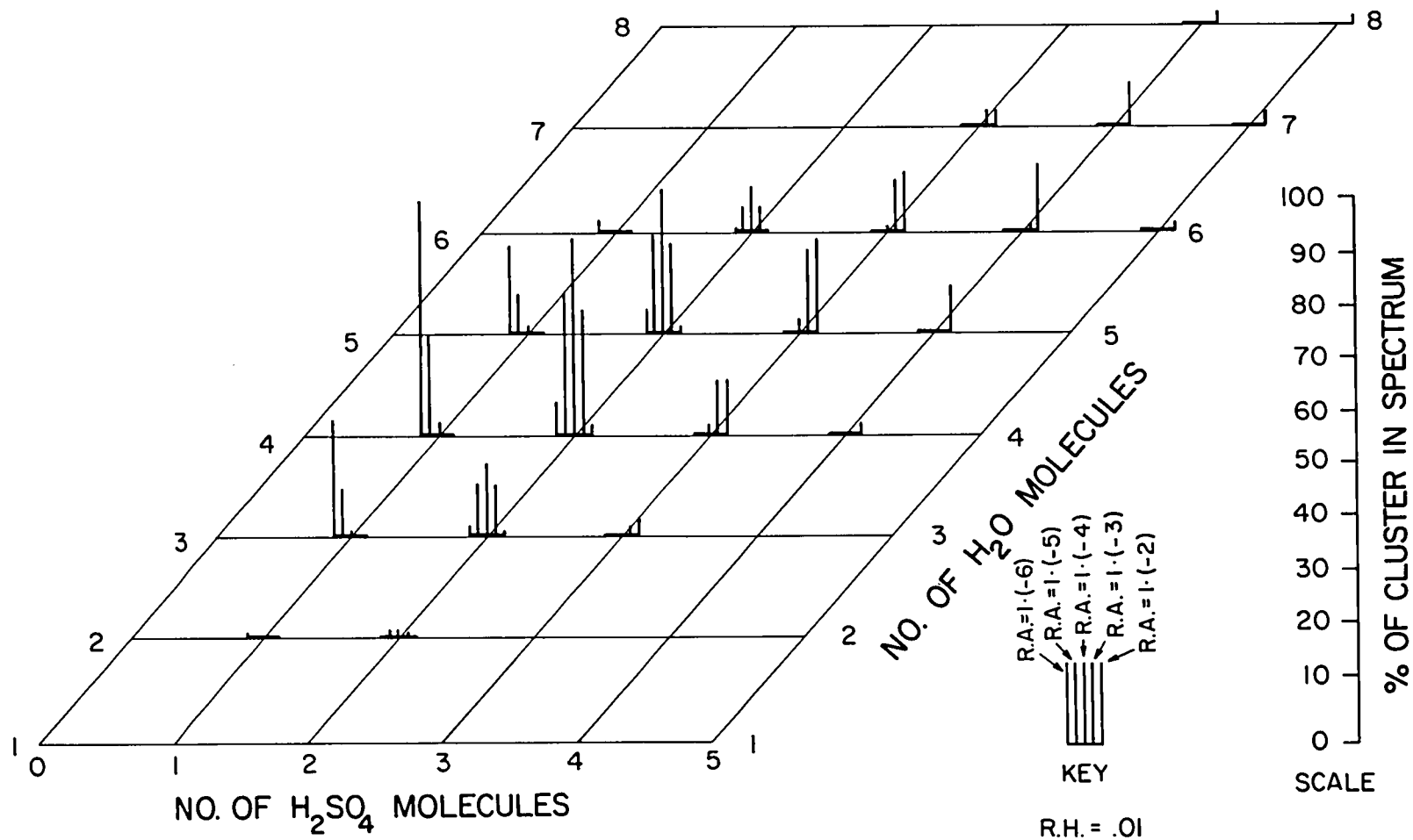


Figure 1.- Effect of change of H<sub>2</sub>SO<sub>4</sub> concentration on microcluster spectrum in ion-induced nucleation for a mixture of water and sulfuric acid vapor at 27°C.

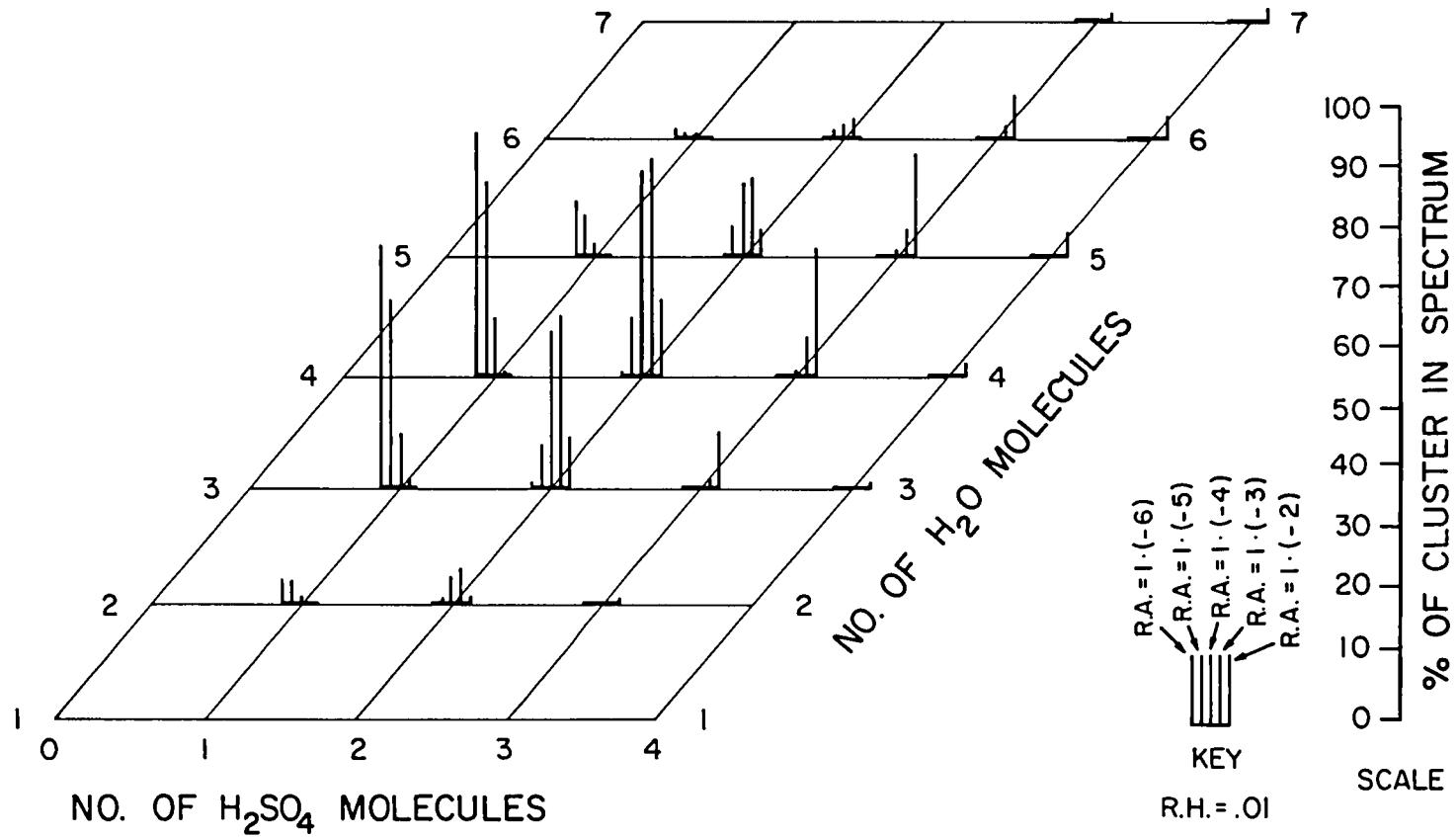


Figure 2.- Effect of change of  $\text{H}_2\text{SO}_4$  concentration on microcluster spectrum in ion-induced nucleation for a mixture of water and sulfuric acid vapor at  $47^\circ\text{C}$ .



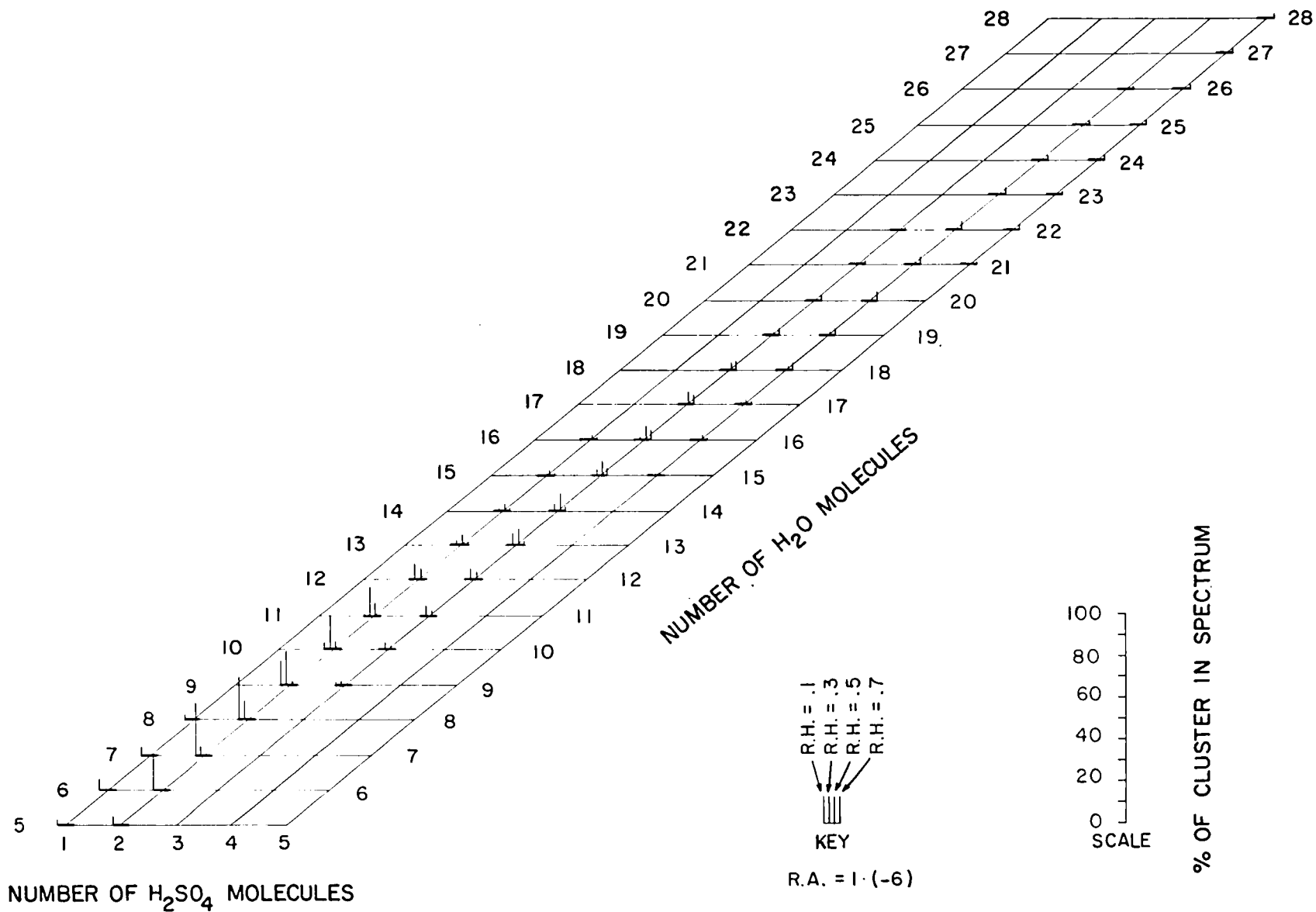


Figure 3.- Effect of a trace of  $H_2SO_4$  on ion-cluster spectrum for various values of relative humidity at low temperature ( $T = 7^\circ C$ ).

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16. Abstract  Thomson's ion-nucleation theory has been modified to include the effects of curvature dependence of the microscopic surface tension; of field-dependent, nonlinear, dielectric properties of the liquid; and of sulfuric acid hydrate formation in binary mixtures of water and sulfuric acid vapors. The modified theory leads to a broadening of the ion-cluster spectrum, and shifts it towards larger numbers of H <sub>2</sub> O and H <sub>2</sub> SO <sub>4</sub> molecules. Whether there is more shifting towards larger numbers of H <sub>2</sub> O or H <sub>2</sub> SO <sub>4</sub> molecules depends on the relative humidity and relative acidity of the mixture. Usually, a broadening of the spectrum is accompanied by a lowering of the mean cluster intensity. For fixed values of relative humidity and relative acidity, a similar broadening pattern is observed when the temperature is lowered. These features of the modified theory illustrate that a trace of sulfuric acid can facilitate the formation of ultrafine, stable, prenucleation ion clusters as well as the growth of the prenucleation ion clusters towards the critical saddle-point conditions, even with low values of relative humidity and relative acidity.					
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