Observation of a transition in the water-nanoparticle formation process at 167 K

S. Bauerecker,a) A. Wargenau, M. Schultzze, and T. Kessler
Institut für Physikalische und Theoretische Chemie, Technische Universität Braunschweig, D-38106 Braunschweig, Germany

R. Tuckermann
Institut für Physikalische Chemie, Universität Göttingen, D-37077 Göttingen, Germany

J. Reichardt
Meteorologisches Observatorium Lindenberg, Deutscher Wetterdienst, D-15848 Tauche, Germany

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Rapid-scan Fourier transform infrared spectroscopy of the vapor/solid formation process of water nanoparticles in the 180–140 K temperature range at thermal-equilibrium conditions is reported. At 167 K a transition in the formation process was observed: the particle volume quintuples and the particle formation time triples within a temperature interval of ±0.4 K caused by the temperature control. The authors interpret this behavior by an abrupt change in the nucleation rate of the H2O monomers in He buffer gas kept at 167 K and 200 mbar. A size and shape analysis of the particles during the formation process was carried out by application of the discrete dipole approximation method which delivers excellent accordance between experimental and calculated mid-IR spectra. Compared to other compact shapes (cube, prolate ellipsoid, and hexagonal prism) the ideal spherical shape fits the experimental spectra best. A distinct change in shape by particle conversion or agglomeration could be excluded to be involved in the formation process. As a possible explanation of the observed phenomenon, a transition from vapor/liquid/solid to vapor/solid nucleation with decreasing temperature is considered which was recently theoretically predicted by van Dongen and co-workers [J. Chem. Phys. 117, 5647 (2002); private communication; J. Chem. Phys. 120, 6314 (2004)]. © 2007 American Institute of Physics. [DOI: 10.1063/1.2713099]

INTRODUCTION

Water nano- and microparticles show a great variety of manifestation due to the dependence of their physicochemical properties on temperature, pressure, structure, and, compared to the bulk matter states, additionally on size and shape.1–3 The nucleation, growth, and further evolution of the particles with all the bifurcations of state, structure, and shape are not sufficiently understood and worth to be investigated. As an example (which plays a role in the present work), it is obvious that there should exist a transition of vapor/liquid nucleation to vapor/solid nucleation if the temperature is varied.4 Vapor/liquid nucleation is well described at temperatures $T > 200$ K.5–7 On the other side, vapor/solid nucleation certainly takes place at temperatures $T \lesssim 100$ K in adiabatic expansions8 and collisional cooling experiments,3 where higher supersaturations and smaller critical nuclei appear. Recently, a theoretical approach to describe the transition between both nucleation paths was given,4 which is just in the process of perfecting.9,10 In the present work, a transition in the nucleation and formation behavior of water nanoparticles has been detected which could meet the predicted conditions.

a)Author to whom correspondence should be addressed. Electronic mail: s.bauerecker@tu-bs.de

EXPERIMENT

To investigate the formation of the water particles, rapid-scan Fourier transform infrared (FTIR) spectroscopy in combination with an optical long path collisional cooling cell11 combined with a pulse-injection sample-gas inlet11–13 was used as an alternative to expansion techniques8,14–16 and cloud chambers.17,18 In general, collisional cooling (compare reviews11,19) is suited to simulate thermal-equilibrium conditions for molecular nanoparticles in natural environment. Our cooling cell, in principle, consists of a vertically oriented cylinder which is filled with a tempered buffer gas and sticks in a Dewar vessel. The cooling agent (cold nitrogen in the present case) encloses the outer cell cylinder. The IR beam is coupled from top into the cell and is multireflected within the cell by White mirrors which are moderately heated (+5 K) to avoid sample-gas deposit on it. The temperature and the pressure of the system can be independently adjusted between 4 and 400 K and between 0.01 and 3000 mbar (or higher, depending on the optical cell’s windows properties) which covers atmospheric and many extraterrestrial basic conditions. For the present investigation a cold gas system, version GKSS of Karlsruher Glastechnisches Werk, which consists of a liquid-nitrogen vaporizer, a heat exchanger, and a PT100 fuzzy-logic controller was used to adjust selected temperatures in the 120–300 K region in the cooling cell. By additional use of the three-zone heating system integrated in
The water sample-gas concentration was regulated with a helium gas flow, which was saturated with water vapor at –20 °C by use of a cryocooler. This corresponds to a water concentration of about 500 ppm in helium at a prepressure of 2000 mbar. The sample gas is pulse injected into the cold buffer gas in the cell forming nanoparticles which are suspended in the buffer gas for minutes up to hours. The injection pulse volume was 100 ml. The pressure was varied between 10 and 900 mbar, however, the nominal pressure was 200 mbar. The infrared spectra were recorded with a Nicolet Magna 550 FTIR spectrometer equipped with a Globar light source, a KBr beam splitter, KBr windows, and an external InSb detector. The optical path length was 20 m. The rapid-scan spectra were recorded with a temporal resolution of 0.54 s over 6 s each at a resolution of 4 cm⁻¹ and were linearly base line corrected. During such relatively short measuring times particle settling does not play a significant role.

Control measurements with an additive of about 1% HDO to the H₂O/He sample gas were carried out at the same experimental conditions. The spectral band of the decoupled HDO molecules acts as a marker for the liquid phase. In this contribution we concentrate on the vibrational combined ν₁, ν₃ region of water ice I spectra, simply termed as water particle spectra in the following. Figure 1 shows the main experimental results of the present work which are discussed in the next but one section.

DISCRETE DIPole ANALYSIS

The infrared spectra shown in the present work are determined by the absorption and scattering of light by water nanoparticles in the aerosol phase with log-normal size distributions. In general, both the shape of the particles and the shape distribution have to be considered. Thus, a preferably nondestructive size and shape analysis is essential to describe the particles and their evolution. For that purpose we use the discrete dipole approximation (DDA) code first described by Purcell and Pennypacker²⁴ and implemented by Draine and Flatau.²¹,²² The code approximates the target, i.e., a single particle, by a cubic array of polarizable oscillator points and allows accurate calculations of electromagnetic scattering from targets with sizes of up to five times the irradiating wavelength.

As an input to the DDA method the frequency-dependent optical constants of water ice, i.e., the complex refractive indices of Clapp et al.,²₅ determined at 190 K from ice aerosol spectra, were used. Application of the optical constants of Warren²₆ at 266 K being far from our main temperature of 167 K does not lead to satisfying results. To fit the experimental spectra, in the calculations the spectra of different particle sizes (using an increment of 10 nm) were superposed for each shape of the particles by weighting them with a log-normal distribution. Via a minimization of the mean square error sum procedure, the median size rₘₑₐ₅ and the standard deviation σ of the best-fitting log-normal size distribution have been calculated for the last spectrum of each series shown in Fig. 1 and each particle shape. As an example for the DDA method, Fig. 2 shows calculated midinfrared spectra of water ice spheres with sizes between 0.1 and 1.0 μm at 190 K.

RESULTS

This presentation focuses on the dependence of the water-nanoparticle OH-stretch mode band spectra (between 2500 and 4000 cm⁻¹) on temperature. The dependence of the midinfrared spectra of the water nanoparticles on the buffer gas pressure in the collisional cooling cell turned out to be not very strong around the nominal pressure of 200 mbar. Within the temperature range between 80 and 165 K, the temperature dependence was smooth in band position and bandwidths, corresponding with the results of Devlin and co-workers. However, at 167 K, within the temperature interval of ±0.4 K, an abrupt change in the final shape of the stretch mode bands of the grown particles as well as in the evolving process itself was found, see Fig. 1. In short, the cooling cell, the temperature could be kept within an interval of smaller than ±0.4 K.

The time step between two spectra is 0.54 s in each series. The temperature was kept at 167 K in each series within the accuracy of the temperature control of ±0.4 K. Series 1 corresponds to the particle evolution behavior at temperatures lower than 167 K, and series 3 to that at temperatures higher than 167 K. Such series for lower and higher temperatures have been measured but are not shown in the present work. Both, the particle size and the particle formation time were determined by the absorption and scattering of light by water nanoparticles in the aerosol phase with log-normal size distributions. In general, both the shape of the particles and the shape distribution have to be considered. Thus, a preferably nondestructive size and shape analysis is essential to describe the particles and their evolution. For that purpose
size of the particles according to the last spectrum of each rapid-scan series almost doubles from 460 nm via 580 nm to 790 nm. The detailed size determination by DDA calculations is discussed below, see Fig. 4 and Table I. The second striking observation in the particle evolution process is that the formation time, here defined as the time needed for the reduction of the monomer absorbance to 10% of its initial value, nearly triples from 1.8 s via 2.7 s to 5.9 s, see Figs. 1 and 3.

In Fig. 3 the conversion from the monomers to particles of each series of Fig. 1 is depicted. The left ordinate describes the integrated absorbance of the diminishing monomers and the right ordinate shows the integrated extinction of the forming water particles over time. The enhancement factor of the integrated extinctions of the nanoparticles compared to those of the monomers is 21 as an average for the three series of Figs. 1 and 3. It results from the strong intermolecular dipole coupling of the O–H bonded molecules in the particles and corresponds to the 25-fold enhancement of the integrated extinctions of the nanoparticles calculated from DDA size analysis for spectra at 0.54, 1.08, and 3.78 s.

### Table I. Optimum fit results of DDA calculations of H₂O particle spectra with particle shapes similar to a sphere fitting theoretical spectra to the experimental final spectra of series 1, 2, and 3 in Fig. 1.

<table>
<thead>
<tr>
<th></th>
<th>Series 1</th>
<th>Series 2</th>
<th>Series 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphere</td>
<td>r_m / nm</td>
<td>458</td>
<td>584</td>
</tr>
<tr>
<td></td>
<td>σ</td>
<td>&lt; 10⁻¹</td>
<td>1.3·10⁻¹</td>
</tr>
<tr>
<td></td>
<td>s</td>
<td>1.6·10⁻⁴</td>
<td>1.1·10⁻⁴</td>
</tr>
<tr>
<td>Ellipsoid, prolate 3:2</td>
<td>r_m / nm</td>
<td>452</td>
<td>594</td>
</tr>
<tr>
<td></td>
<td>σ</td>
<td>&lt; 10⁻¹</td>
<td>9.2·10⁻²</td>
</tr>
<tr>
<td></td>
<td>s</td>
<td>2.3·10⁻⁴</td>
<td>1.4·10⁻⁴</td>
</tr>
<tr>
<td>Cube</td>
<td>r_m / nm</td>
<td>428</td>
<td>593</td>
</tr>
<tr>
<td></td>
<td>σ</td>
<td>1.2·10⁻¹</td>
<td>9.2·10⁻²</td>
</tr>
<tr>
<td></td>
<td>s</td>
<td>2.2·10⁻⁴</td>
<td>1.4·10⁻⁴</td>
</tr>
<tr>
<td>Prism, hexagonal 1:1</td>
<td>r_m / nm</td>
<td>441</td>
<td>594</td>
</tr>
<tr>
<td></td>
<td>σ</td>
<td>8.8·10⁻⁴</td>
<td>1.0·10⁻¹</td>
</tr>
<tr>
<td></td>
<td>s</td>
<td>2.3·10⁻⁴</td>
<td>1.4·10⁻⁴</td>
</tr>
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</table>
of the oscillator strength described in the literature\textsuperscript{19,27} for the increase from water monomers to molecules bound in ice I.

Figure 4 shows the final spectra of the three rapid-scan series of Fig. 1 at 3.78, 4.32, and 4.86 s in comparison with DDA calculated spectra of spherical water ice particles with radii of 460, 600, and 800 nm (the computational increment was 10 nm, the full hundreds are accidental). The scattering fraction increases from 28.8\% and 43.9\% to 56.9\%. In this calculations only one parameter, the particle radius, is varied and optimized. That means we use a monodisperse size distribution here. The agreement of the experimental and calculated spectra is excellent. Furthermore, the scattering and absorbance fractions of the extinction spectra are displayed (dotted curves). The scattering fraction (left band structure in each case) increases from series 1 to series 3 from 28.8\% via 43.9\% to 56.9\%.

FIG. 4. (Color online) Comparison of the final experimental spectra depicted in the series in Fig. 1 (solid lines) with DDA calculated spectra (dashed bold lines). In contrast to the calculations summarized in Table I, here only one parameter (apart from the linear base line correction of the experimental spectrum)—the particle size—was varied to demonstrate the dominant role of this parameter. The shape of the particles was assumed to be spherical. Agreement between experimental and calculated spectra is excellent. Furthermore, the scattering and absorbance fractions of the extinction spectra are displayed (dotted curves). The scattering fraction (left band structure in each case) increases from series 1 to series 3 from 28.8\% via 43.9\% to 56.9\%.

**DISCUSSION AND CONCLUSIONS**

To explain the observed abrupt change in the water-nanoparticle formation process at 167 K, the following phenomena will be discussed as a cause or at least to be involved in the transition: change of particle shape, agglomeration of the particles, change of particle structure, and a sharp increase in the nucleation rate.

**Change of shape.** The dependence of the shape of bigger water ice particles (e.g., appearing as hexagonal plates, needles, hollow columns, and prisms) on temperature and supersaturation is a well investigated phenomenon at higher temperatures than 200 K.\textsuperscript{1,28,29} Therefore, the occurrence of different shapes of the particles (with varying relative surfaces and local vapor pressures) should also be taken into consideration for the formation process of smaller particles at lower temperatures between 160 and 200 K. This emphasizes the importance of an accurate shape analysis of the particles in order to detect such possible different shapes. However, according to the above presented results, the forming water particles have spherical shape during the formation process over about 5 s, rather than other shapes.

Particle agglomeration. Generally, aerosol particles smaller than 1 μm collide as a result of their Brownian motion.\textsuperscript{18} In consequence, a temperature dependent “sticking ability” of the particles in our experiment has to be considered to explain the transition. As a necessary property for water-particle agglomeration in clouds\textsuperscript{1} and acoustic

**FIG. 5.** (Color online) Comparison of spectral band shapes of H\textsubscript{2}O particles with different shapes (sphere, cube, bar, and disk) with volume-equivalent radii of 800 nm. The spectra were calculated with the discrete dipole approximation code. Averaging over all orientations has been done for all shapes apart from the spherical. Note that the DDA spectrum of the sphere cannot be reproduced by assuming a different shape (hexagon and cube) and by varying the equivalent radius in the calculations. This finding permits the detection of the underlying particle shapes.
fields, a quasi-liquid-layer (QLL) on the water particle surfaces has been discussed. Therefore, a QLL could also play a role in Brownian-motion driven sticking processes. But in turn, we can argue against such a process with the observed stable spherical particle shape which should change towards dendritic three-dimensional lattices or towards more compact but irregular structures if noticeable agglomeration would occur. This is supported by further DDA calculated spectra for the three series which indicate a particle growth driven by vapor-solid conversion and not by agglomeration, compare Fig. 3. Further evidence is given by a simple estimate of the time which is needed to reduce the particle concentration to 90% by coagulation of the particles. For the conditions described in the experimental part, the water-nanoparticle concentrations in the cooling cell are roughly between $10^5$ and $10^7$ cm$^{-3}$ for the three series. If we assume a monodisperse distribution of particles with around 50 nm in size or bigger and that every collision (which is driven by Brownian motion) led to coagulation of the particles, then this reduction time is in the region of several minutes up to hours for our experimental conditions. This is far beyond the measuring time of 6 s, see Fig. 3. So we can exclude that particle agglomeration is a significant effect and a cause for the transition. However, the occurrence of a QLL in the reported experiments cannot be excluded in general.

Cubic phase. As the water particles of Figs. 1, 3, and 4 reach final radii of 450–800 nm, most of their molecules are four coordinated in a quasi-bulk-phase of water. At temperatures below 180–190 K the cubic phase commonly forms and exists as a metastable structure of bulk ice I, while at temperatures below 180–190 K the cubic phase commonly forms and exists as a metastable structure of bulk ice I. This suggests that the formation of cubic ice under atmospheric conditions forms and exists as a metastable structure of bulk ice I, while at higher temperatures the hexagonal phase prevails. Recent laboratory experiments demonstrate that micrometer-sized liquid droplets freeze to cubic ice under atmospheric conditions below 190 K. This suggests that the formation of cubic ice could also be possible in our experiments in principle. Unfortunately, both structures of ice cannot be distinguished by infrared spectroscopy. Furthermore, at 167 K, cubic ice is estimated to have a vapor pressure of 4%–13% higher than hexagonal ice. In our experiments we have the higher monomer concentration in the series corresponding to higher temperatures (series 3) which could be a hint that a sharp increase in the vapor pressure is involved in the observed transition. However, we cannot accurately measure vapor pressures in our experiment and therefore no clear conclusions can be drawn from this observation.

Nucleation rate. The total amount of water molecules within the optical path (monomers plus nanoparticles) is comparable for the three spectra series in Figs. 1, 3, and 4. As the particle growth is fed by vapor-solid conversion and not by particle agglomeration, the final number and size of the particles are determined by the initial number of nuclei and the total amount of water input. The latter was the same for the three series. The situation is similar to that of nucleation pulse experiments carried out for the determination of homogeneous nucleation rates. From the size of the particles, it can be estimated that in the first series five times, and in the second series 2.4 times, more nuclei were formed in total as in the third spectral series. To explain this increase of the order of two to five in the number of generated nuclei with a temperature interval $\leq 0.8$ K, we suggest a possible transition from vapor/liquid/solid to vapor/solid (after 6 s the water vapor reservoir, i.e., the monomers, has been nearly depleted). Such an effect was theoretically predicted by Peeters, Gielies, and van Dongen and is just in the process of improvement. As a cautionary note, we have not directly observed the liquid phase so far by rapid-scan spectroscopy with a time resolution of 0.54 s. Therefore, if the liquid phase is really involved in the nucleation and formation process it should take place in the first five-tenths of a second.

Summarizing, an optical longpath collisional cooling system which combines fine adjustment of the thermodynamic conditions with time-resolved IR probing of particle size and shape was used to monitor the formation process of water nanoparticles at subfreezing temperatures. A pronounced change in the particle formation behavior was found at 167 K which corresponds to a sharp increase in the nucleation rate with temperature. At the present state of investigations the authors see the transition from vapor/liquid/solid to vapor/solid nucleation with decreasing temperature as predicted by van Dongen and co-workers as the most promising explanation. Very recently, two of the authors could observe a similar transition with NH$_3$ nanoparticles at about 111 K.

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9. V. Holten and M. E. H. van Dongen (private communication).