Modelling of water clusters formation processes in the inner atmosphere of comets

N Y Bykov, D V Leshchev
Center for Advanced Studies, St. Petersburg State Polytechnical University, 195251 St. Petersburg, Politechnicheskaja, 29, Russia
E-mail: nbykov2006@yandex.ru

Abstract. The model of water clusters formation has been developed for the direct simulation Monte Carlo method. The model describes hierarchy of reactions which lead to growth and decay of water clusters including initial processes of dimer formation by triple and binary collisions of water molecules. The algorithm takes into account internal state of clusters and energy exchange processes accompanying clusterization kinetics. The model was applied for the research of condensation process in the rarefied flows of water molecules typical for the inner atmospheres of comets.

1. Introduction
The kinetics of molecular clusters formation is of great interest for large number of applications in science and technology. In particular, the formation of clusters in water vapor flows is a very important process in planetary science. Recently European Space Agency (ESA) approved new research mission Rosetta with 67P/Churyumov-Gerasimenko comet (67P/C-G) as a primary target. Rosetta will rendezvous with the Jupiter family comet 67P/C-G in 2014 and provide the probe landing at the comet surface. Preliminary estimations of near-nucleus atmosphere parameters affected strongly by water clusters formation processes [1] are required for landing mission success and correct interpretation of observations results.

The aim of present research is to formulate the model water clusters growth and to research cluster formation phenomenon for the flows in inner atmosphere of 67P/C-G comet. For numerical investigation we employed the direct simulation Monte Carlo method (DSMC) [2] which widely used for modeling of rarefied and near-continuum flows with different physic-chemical processes in volume.

2. Kinetic model of water clusters formation
The model of clusters formation has been elaborated recently for the DSMC method [3,4]. The clusters are characterized by number of monomers \( k \), mass, radii (determined by modified drop spherical model [3]), translation velocity, rotation and vibration degrees of freedom and corresponding rotation and vibration internal energies. For description of vibration state of water cluster we use traditional presentation of vibration energy [2]

\[
E_{v,k} = \sum_{i=1}^{3k-6} \left( \frac{k_B \theta_i}{\exp[\theta_i/T]-1} \right)
\]
where $\theta_i=h\nu_i/k_B$ — characteristic temperature of vibration mode $i$ ($h$ — Plank constant, $\nu_i$ — vibration frequency of mode $i$), $k_a$ — number of atoms (H and O) in cluster, $T$ — temperature. The known data on frequencies of inter- and intra-molecular vibrations of water clusters are generalized in [3]. The use of (1) gives possibility to calculate effective excited vibration degrees of freedom and to take into account partial excitation of vibration internal modes.

$$
\begin{align*}
\text{i} & \quad H_2O + H_2O + H_2O \rightarrow (H_2O)_2 + H_2O^* \\
\text{ii} & \quad H_2O + (H_2O)_k \rightarrow (H_2O)_{k+1} \\
\text{iii} & \quad (H_2O)_{k_1} + (H_2O)_{k_2} \rightarrow (H_2O)_{k_1+k_2} \\
\text{iv} & \quad (H_2O)_{k+1} \rightarrow H_2O + (H_2O)_k \\
\text{v} & \quad H_2O + H_2O \rightarrow (H_2O)_2
\end{align*}
$$

where $p, p_i, a_i$ — probabilities of reactions.

In general case [3] the model takes into account such kinetic processes as (i) dimer formation under triple collision of monomers, (ii) reaction of the monomer-cluster association under binary collisions of these particles, (iii) reaction of the cluster-cluster association under mutual collisions of clusters, (iv) cluster decay by one monomer evaporation. For the conditions of low temperature flow of water molecules the probabilities of association during particles collisions for reactions (i)-(iii) were supposed to equal 1 [3]. The new feature of the developed model for water clusters formation is in consideration of additional reaction (v) which allow to form dimer directly under binary collision of water molecules. Opposite the case of atomic dimer formation, for our problem this reaction may take place due to enough large capacity of vibration modes of water dimer. For the water vapor flows in inner comet atmospheres the probability of monomers association under binary collisions of water molecules was estimated to be $p=0.01$ [1]. We use also alternative way for $p$ determination based on approach discussed in [5] for estimation of probability association of atoms under triple collisions. This approach predicts for reaction (v)

$$
p = CE_{es}^x, x = b - 0.5, C = \frac{a\sqrt{m_r}}{k_B^b\sigma_f^{1/2}} \frac{\Gamma(\zeta_c/2)}{\Gamma(b - 0.5 + \zeta_c/2)}
$$

where $E_{es}$, $\zeta_c$, $m_r$ — total energy, total number of degrees of freedom and reduced mass of collision pair correspondently, $\sigma_f$ — collision cross-section (for hard spheres model), $\Gamma$ — gamma-function, $a$ and $b$ — constants in Arrenius type equation for the rate of association reactions without activation barrier: $k_{ass}=aT^b$. The data about $a$ and $b$ constants are very poor. The estimations [6] give $a$ in the range $10^{10}$–$10^{14}$ cm$^3$/mole s, $b=0$.

3. Statement of the problem

Under orbital motion of comet 67P/C-G the maximal flux of water molecules through active areas of nucleus $Q$ is observed in perihelion (1.29 AU from the Sun) and is approximately $10^{33}$s$^{-1}$ [7]. The usual approach to model flow in near nucleus comet atmosphere is in simplification of the problem toward 1D spherical setting [1]. In this case the nucleus characterized by effective radius $R_{eff}=(\beta S)^{1/2}$, ($S$ — is the total surface area, $\beta=0.05$ — the ratio of an active area to the total area of the surface) [7]. Below we present simulation results for the case of expansion of water molecules in vacuum evaporated at rate $Q$ from the sphere with $R_{eff}=900$ m. The surface temperature was $T_{suf}=200$ K, this value was estimated for equatorial parts on the base of the thermal model of a porous ice nucleus [8]. The considering flow region was $R_{eff}<X<3R_{eff}$. The probability of association of water molecules under binary collisions (reaction (v)) was $p=0.01$ (case 1) or determined by equation (2) with parameters $a = 10^{12}$ cm$^3$/mole s, $b=0$ (case 2) and $a = 10^{10}$ cm$^3$/mole s, $b=0$ (case 3). The last one may be
considered for estimation of minimal degree of condensation process in the comet atmosphere. Other details of the problem setting and parameters of the DSMC method are the same as in [3].

4. Results and discussion

For considering range of initial parameters the characteristic Knudsen number was \( \text{Kn} = \lambda_w / R_{eff} = 0.2 \times 10^{-4} \) (\( \lambda_w \) — free path near the surface). This value corresponds to near continuum flow regime. The data on the degree of supersaturation in such flow predict good conditions for cluster formation process (Figure 1a).

The degree of condensation may be defined as

\[
\alpha_s = \sum_{k=2}^{\infty} k N_k / \sum_{k=1}^{\infty} k N_k
\]

where \( N_k \) — the total number of clusters with size \( k \) in the considering flowfield. For the cases 1 and 2 \( \alpha_s = 0.23 \) and 0.21 accordingly. For case 3 the ratio of association process (\( \nu \)) is less by two orders of magnitude in comparison with case 2. Nevertheless, the value of \( \alpha_s \) for this case is surprisingly high (\( \alpha_s = 0.13 \)). The influence of water clusters formation processes on gasdynamic parameters is very high (Figure 1). The density of monomers-clusters mixture drops more quickly in comparison with the flow without condensation. In most area of the flow values of temperature for the case 1 differ from the case without clusterization approximately in five times. The reason of this fact is in release of latent heat of condensation during clusters growth process. The velocity of the flow is also affected by clusterization and sufficiently higher in comparison with flow without cluster formation process.

The clusters formation process starts in the vicinity of the nucleus surface. The role of triple collisions of water molecules (reaction (i)) on the dimer formation process is negligible. The most probable way of dimers appearance in the inner atmosphere of 67P/C-G comet is under binary collisions of water molecules. The maximal value of clusters density is near the nucleus surface, with increase of the distance from the nucleus density drops (Figure 1a). The employed model of cluster formation predicts close velocities of small clusters, monomers and the gas mixture in the considering near-surface region (Figure 1b).

The size distributions of forming in whole flowfield water clusters are presented in Figure 2. The majority of water clusters is dimers for cases 1 and 2. For low rates of association process (case 3) the

![Figure 1a](image1a.png)

![Figure 1b](image1b.png)

**Figure 1** a: radial distributions of density (1) and degree of supersaturation \( S \) (2) of gas for case without condensation, density of gas mixture (3) and clusters with size \( k=10 \) (4) for case 1. b: radial distributions of velocity (1) and temperature (2) of gas for the case without condensation, velocity(3) and temperature(4) of gas mixture, velocity of clusters with size \( k=10 \) (5) for case 1. \( \rho_0 = 9.9 \times 10^{-7} \text{ kg/m}^3 \)

The size distributions of forming in whole flowfield water clusters are presented in Figure 2. The majority of water clusters is dimers for cases 1 and 2. For low rates of association process (case 3) the
small clusters in the range $2<k<10$ have got approximately the same representation. The difference between considered cases with intensive condensation (cases 1 and 2) and week rates is very large for clusters with sizes $2<k<20$. For all cases the maximum size of observed clusters exceeds 150 molecules per cluster.

**Figure 2.** Total over flowfield size distributions of clusters. 1 — case 1, 2 — case 2, 3 — case 3

**References**

[1] Crifo J F 1990 Water clusters in the coma of comet Halley and their effect on the gas density, temperature, and velocity *Icarus* **84** 414

[2] Bird G A 1994 *Molecular gas dynamics and the direct simulation of gas flows* (Oxford: Clarenton Press)

[3] Bykov N Y 2009 Modelling of condensation at spherical expansion of water vapor into vacuum *Thermophysics and Aeromechanics* **16** 177

[4] Li Z, Zhong J, Levin D A, Garrison B J 2009 Kinetic nucleation model for free expanding water condensation plume simulations In *Proc. of 26th int. symposium on RGD (AIP Conference Proceedings 1084, American Institute of Physics, Melville, NY)* ed Takashi Abe, pp. 613-618.

[5] Bykov N Y, Leshchev D V, Simakova O I 2008 The direct simulation Monte Carlo of near-continuum flows with condensation process, In *Proc. of XXXVI summer school Advanced Problems in Mechanics ( Saint-Petersburg: Comilfo)* pp. 159-166

[6] Physic-chemical processes in gasdynamics 1995 Handbook, I, ed Chernyi G G, Losev S A, (Moscow: Moscow state university press)

[7] P.L. Lamy, I. Toth, B.J.R. Davidsson, et al. 2007 A portrait of the nucleus of comet 67P/Churyumov-Gerasimenko *Space science reviews* **128** 23

[8] M.C. De Sanctis, M.T. Capria, A. Coradini 2006 67P/Churyumov-Gerasimenko nucleus model: Portrayal of the Rosetta target *Advances in space research* **38** 1906