Proceedings of RGD20

KINETIC THEORY OF PHOTOSTIMULATED NUCLEATION

Andrey L. Itkin,
(International Institute for Problems of the Asteroid Hazard, Russia; Apt.37, Taganskaya 44, Moscow, 109147, Russia, itkin@momipao.msk.su)

ABSTRACT: The plausible ways to influence the condensation rate and properties of the forming clusters by radiation are discussed. One of them is photostimulated nucleation which kinetic model has been proposed in [1]. This theory disregards photochemical reactions accounting only for excitation of electronic states of molecules and clusters and allows naturally to explain the available experimental data. The influence of IR on the condensation is also discussed.

1 INTRODUCTION

In this report we discuss plausible ways to influence the condensation rate and properties of the forming clusters by radiation. The first one is photonucleation that has been observed in many experiments (for instance, see [2] and bibliography in [3]) where the rate of water vapor, some aldehydes and carbon dioxide condensation is dramatically accelerated in the presence of the resonance UV radiation. However, hitherto there has been no an agreed-upon viewpoint or an adequate theory of such processes. The difficulty of theoretical interpretation of the data obtained lies in the fact that in various systems both physical and chemical mechanisms of complex formation can manifest themselves while the system *per se* may have homogeneous as well as heterogeneous composition. Probably, this is the reason that despite numerous attempts, no unified mechanism of photonucleation has been established. All this has resulted the authors of [4] in the conclusion that the mechanism should be associated with concrete values of the wavelength λ and intensity I of radiation and be essentially determined by the composition of the system under consideration.

The available semiphenomenological models provide a qualitative description of some experimental results. One of them considers the "radical" mechanism involving photodissociation of the initial compound and formation of complexes in chemical reactions with participation of radicals. Another model implies the formation of heterogeneous complexes of the electron-excited molecules of the initiating substance with molecules of condensed vapor. Thus, some additional problems are introduced into these models which are inherent to modern theories of binary nucleation. The absence of more consistent models is usually accounted for by the necessity of consideration of the internal structure of clusters, analysis and solution of related kinetic equations which as it is known brings problems as well as by the lack of data on rate constants of formation, decomposition and relaxation of excited clusters.

In [1] we utilized a generalization of our microscopic condensation theory (MCT) to analyze photonucleation under certain suppositions of the mechanism of this process, and in [3] the transfer processes in a thermal diffusion chamber under photostimulated nucleation were examined. Here based on these papers we discuss the kinetic mechanism of photonucleation suggested in [1]. To eliminate difficulties encountered when treating the binary nucleation, we consider simple systems such as $CS_2 - He$ and $H_2O - Ar$, for which the absence of radicals and heterogeneous complexes during photonucleation has been proved [2, 4].

2 STATEMENT OF THE PROBLEM

Peculiarities of the photonucleation kinetics firstly we shall consider representing the condensible gas as a mixture of ideal gases of molecules and clusters. Throughout the observation time this system interacts with radiation of constant intensity I and frequency ν. Since according to the data of the

authors mentioned in introduction photonucleation is observed at values of ν corresponding to the electron absorption spectrum of monomers we shall restrict ourselves only by these frequencies. Of a diversity of processes occurring in such a system, decisive are considered the ones presented below and grouped according to the scheme

Unexcited clusters		**Excited clusters**
1. condensation	2. relaxation	6. condensation
$A_1 + A_1 \leftrightarrow A_2(k)$, $A_j(k) + A_1 \leftrightarrow A_{j+1}(l)$, $k = 0...M_j, l = 0...M_{j+1}$, $j = 2...N-1$	$A_j(k) + A_1 \leftrightarrow A_j(l) + A_1$, $A_j(k) + A_1^* \leftrightarrow A_j(l) + A_1^*$ $k, l = 0...M_j, j = 2...N$	$A_1 + A_1^* \leftrightarrow A_2^*(k)$, $A_j(k) + A_1^* \leftrightarrow A_{j+1}^*(l)$, $A_j^*(i) + A_1 \leftrightarrow A_{j+1}^*(l)$, $i, l = 0...M_j^*, k = 0...M_j$,
3. monomer excitation	4. cluster excitation	7. relaxation
$A_1 + A_1 \leftrightarrow A_1 + A_1^*$, $A_j(k) + A_1 \leftrightarrow A_j(l) + A_1^*$, $k, l = 0...M_j, j = 2...N$	$A_j(k) + A_1 \leftrightarrow A_j^*(l) + A_1$, $A_j(k) + A_1^* \leftrightarrow A_j^*(l) + A_1$, $k = 0...M_j, l = 0...M_j^*$,	$A_j^*(k) + A_1 \leftrightarrow A_j^*(l) + A_1$, $k, l = 0...M_j^*, j = 2...N$
5. photoexcitation		
$A_1 + h\nu \leftrightarrow A_1^*$, $k = 0...M_j, l = 0...M_j^*$,	$A_j(k) + h\nu \leftrightarrow A_j^*(l)$,	

Group 1 describes formation of clusters from monomers being in the ground electronic state A_1 and their decay when the cluster vibrational energy $E_j(k)$ can change up to $E_j(M_j)(M_j$ is the number of the topmost level still enabling one to consider a bound state of all j monomers of cluster A_j. Group 2 includes the processes of VRT exchange upon collision of clusters with ground-stated and electron-excited monomers (A_1^*). A unitary excited monomer A_1^* may be formed at collision of "hot" monomers with clusters and other monomers (Group 3) or under the action of external radiation (Group 5). The same radiation can also excite one of the monomers involved in a cluster resulting in formation of the excited cluster A_j^* (Group 5). Both a unitary excitation of a few monomers in a cluster or a multiple excitation of monomers are neglected. Group 4 comprises reactions of formation of excited clusters at collision of A_j with "hot" monomers. Groups 6 and 7 are analogous by their sense to Groups 1 and 2 and describe condensation and VRT relaxation of excited clusters. Here we neglect the probability of collision of two clusters or any two excited particles assuming their concentration to be too small.

Formulating the set of equations describing the above listed processes we assume that all gases of monomers and clusters have unified translatory-rotational temperature T. The state of the mixture will be given by sets $x_j(k)$ and $x_j^*(k)$ defining the numerical densities of clusters consisting of j molecules with the internal vibrational energy $E_j(k)$ in the ground or excited state, respectively. These populations are normalized to concentrations and the concentrations to a total number of monomers in the system. A set of kinetic equations describing the evolution of populations in the reactions of Groups 1-7 is given in [1]. However, these equations are extremely complicated to be solved directly because of its large dimension and the absence of data for the most rate constants. Nevertheless, they can be simplified with the help of special asymptotic procedure proposed in [1]. It finally results in an analytical solution both for populations and concentrations of clusters presented the explicit functions of temperature T and supersaturation S. Thus, instead of the initial infinite system of coupled differential equations one should solve the only kinetic equation for S further analytically

restoring the cluster size distribution function. With a good accuracy it is possible to write this equation in the following form

$$\frac{dS}{dt} = -S^{x+2}\Theta_x \prod_{i=1}^{x} \Theta_i C_{x+1} n_{x+1,e} \frac{b}{9x^{-4/3}} \tag{1}$$

Here n_{je} is the equilibrium concentration of j-cluster [5]; C_j in a physical sense is a rate constant of formation of j-cluster from $j-1$ one by attaching a monomer, which really is a certain complex function of T, I and S; x is the root of the equation

$$(S\Theta_j)^{-1}\left(1 - \frac{b}{3j^{1/3}}\right)\exp\left(\frac{2b}{3j^{1/3}}\right) = 1 \tag{2}$$

with j being the number of molecules in a cluster, $b \equiv 4\pi\sigma\eta^2/k_BT, \eta = (3m/4\pi\rho_l)^{1/3}$, σ is the surface tension, m is the mass of the monomer, ρ_l is the liquid density, k_B is the Boltzmann constant.

As far as Θ_j is concerned it is a complex function of T and I which is given in [1]. At $I = 0$ one has $\Theta_j = 1$. For us it is only important that Θ_j shows a weak dependence on j ($\Theta_j \approx \Theta$), that yields $x \approx (b/3lnS\Theta)^3 = j^p_{*,cl}/8$, where $j^p_{*,cl}$ is the analog of the classical critical size $j_{*,cl}$. If we introduce a new supersaturation $S_p = S\Theta$ then $j^p_{*,cl} = (2b/3lnS_p)^3$, i.e. it is determined like $j_{*,cl}$. Certainly, $j^p_{*,cl} = j_{*,cl}$ at $\Theta = 1$.

As discussed in [1] it is reasonable to assume that the most effective processes of the cluster formation are those in which the attachment of the excited monomer to the neutral cluster occurs. It allows to show that $\Theta \sim I$ and $\Theta \gg 1$ at the moderate I. Thus, the later is well executed in the photonucleation experiment. In particular, for S_2 vapors with $\lambda = 300nm, I = 10^{-4}W/m^2$, the energy defect between the ground and the first excited states of the monomer - $\Delta\epsilon_{10} = 20ev$ [2], this condition is well met. In view of this even at $S = 1$ and moderate I, x is not a very large value, though at $I = 0$ ($\Theta = 1$) and $S = 1$ one has $x \to \infty$. Then from (1) it is possible to get at $S = const$

$$\ln(dS/dt) \approx const + (x+2)lnI$$

This relation has been analyzed in detail in [3] where it is shown that it qualitatively describes the available experimental data. A close relation can be obtained also for the rate of evolution of cluster concentrations n_j

$$\ln\, dn_j/dt|_{S=const} \approx const + (2x+2)lnI \tag{3}$$

3 ANALYSIS OF THE EXPERIMENTAL DATA

Nowadays the most customary tool for studying photonucleation is the thermal diffusion chamber described in detail in [6]. This apparatus has frequently been utilized for investigating the homogeneous nucleation of various substances. The features of photonucleation begin to be observed if a beam of monochromatic UV light is aimed at the point of maximum supersaturation. It has been found that an increase in the beam intensity I is accompanied by a sharp increase of the nucleation rate, the critical supersaturations are characterized by unprecedentedly low values. Investigations carried out for a number of substances (see [8, 2] and references in these papers) made it possible to establish several general laws. It has been discovered that for fixed values of S and I the dependence of the

nucleation rate J on the radiation wavelength λ coincides with a picture of the absorption spectrum in the field of electronic transitions of the monomer; at $S = const$ and $\lambda = const$ one has $J \sim I^n$, where the values n lie on the range 1 - 10 [8]; with λ growth in order to satisfy the condition $S = const$ it was necessary to increase I under a linear law. However, deviations from this relations were also observed. Thus, for water vapor a strong influence of radiation on the condensation rate at wavelength $\lambda = 280 - 340$ lying beyond the edge of the electron spectrum of the water molecule ($\simeq 180$) [2] has been found out. A greater increase in λ leads to predissociation of clusters and the condensation rate falls [9].

By virtue of the design features of TDC the thickness δ_{uv} of the zone in which UV radiation interacts with the vapor-gas mixture filling the chamber, is small ($\delta_{uv}/H \ll 1$, where H is the height of the chamber). The experimental conditions are usually so chosen that outside of this zone supersaturation S is practically equal to unity and condensation is not there observed. Moreover, in the absence of radiation under the chosen conditions condensation is not observed anywhere in TDC.

Since the vapor concentration in the chamber is low as compared with the concentration of the carrier gas n_n, the condensation or photonucleation processes do not practically affect the distribution of temperature and pressure over the height of the chamber, which is determined only by the boundary conditions at the walls and by n_n. The distribution of these parameters over the height of the chamber ξ (usually reckoned from the bottom plate) in the stationary case can be found by solving the stationary diffusion and heat conduction equations and is assumed to be known. Moreover, it can be shown that the temperature $dlnT/d\xi \approx 10^{-4} - 10^{-3} cm^{-1}$ and the pressure gradients are small as compared with gradients of the cluster concentrations and in the first approximation may be neglected.

The analysis of the nucleation kinetics in TDC in the absence of UV is given in [10] and can be adopted here if we consider that an active condensation occurs at the vicinity of the ultraviolet beam influence. It results in the following expression for the nucleation rate

$$J = \frac{\delta_{uv}\rho}{\Delta m} \sum_{j>j_0} \frac{1}{j} \frac{d}{d\xi} \left[D_j \frac{d\alpha_j}{d\xi} \right] = \frac{\delta_{uv}}{\Delta} \sum_{j>j_0} \frac{d}{d\xi} \left[D_j \frac{dn_j}{d\xi} \right] \tag{4}$$

Number j_0 denotes the size of clusters enable to scatter radiation of the wavelength λ which is produced by the detecting laser if the start of nucleation is determined by the method of the light scattering. Thus

$$j_0 = (\lambda/2)^3 4\pi\rho_l/3m$$

For visible light $j_0 \approx 10^{12}$, i.e. in the experiment only very large clusters can be detected. Let us remind that in accordance with [3] values of the diffusion coefficient D_j and n_j relate to the zone where the ultraviolet beam crosses the chamber but not to the zone of the cluster registration.

We could take the final solution for n_j [1] and substitute it to (4) taking into account that number j_0 is large enough as compared with x because the product $S\Theta$ is more than unity even for $S \sim 1$ in view of the inequality $\Theta > 1$ at the moderate I. Thus, we get once again relationship (3).

Further we show that (3) reproduces the experimentally observed dependence $\ln J = \gamma(S,T) + \alpha(S,T) lnI$ which has been found in [2] where values α for various S and T are listed in Tab.1. We shall notice that the way of α definition (in [2] two different approaches to measure α has been utilized) strongly influences the final result. Values of x listed in Tab.1 have been obtained by identifying of the parameter α in [2] to the factor $2x + 2$ in (3). As shown in [3] with a good accuracy it is possible

to consider that the dependence of x upon I in a range of I variation in the quoted experiments is weak enough. Thus, for clusters registered in the experiment the logarithm of the condensation rate linearly grows with growth of the logarithm of the radiation intensity at the moderate I and $S = const$, $T = const$. Similarly the logarithm of the rate of the supersaturation variation linearly grows with the growth of $\ln I$ at $S = const$ and $T = const$. With S and T growth the inclination of

Table 1: Coefficients of dependence $\ln J = \gamma(S,T) + \alpha(S,T)lnI$ experimentally detected in [2] for various S and T.

S	T, K	α	x	$b/3x^{1/3}$
3.134	295.06	2.05 ± 0.07	0.025 ± 0.035	8.67
2.756	297.53	2.51 ± 0.07	0.255 ± 0.035	4.01
2.498	300.29	3.63 ± 0.09	0.815 ± 0.045	2.72
2.257	302.29	3.91 ± 0.14	0.955 ± 0.07	2.57
2.016	306.07	6.07 ± 0.12	2.035 ± 0.06	1.99
1.797	309.42	7.94 ± 0.15	2.970 ± 0.075	1.76

this line decreases. Indeed, it possible to show from the definition of x that $\partial x/\partial T \mid_S < 0$. At strong variations of I, on the contrary with an increase of lnI the logarithm of the nucleation rate falls. Such a situation takes place at $x > 1$. In case of $x < 1$ one has $\alpha = 2$ and a linear dependence of $\ln J$ upon $\ln I$ is still valid.

Note that the linear dependence $\ln n_1 = const - lnI$ has been discovered in [11] at $T = const$ where photonucleation of pure CS_2 was studied and relationship (3) meets these data. Also the linear dependence of the logarithm of the nucleation rate upon lnI as well as a reduction of its inclination with T and S growth are qualitatively confirmed by the experimental data on photonucleation of water vapor [2].

In conclusion it should be noted that the developed theory permits to explain the dependencies really observed in experiments on photonucleation under a certain number of the assumptions made here on the character of physical processes in such systems. The attempts of the authors to achieve such the consent of the theory with experiments at other physical assumptions were not successful.

4 THE OTHER WAYS TO CONTROL CONDENSATION

Another way to decelerate condensation is an excitation of intermolecular vibrational states of clusters by resonance IR giving rise to the cluster decay. The method similar to the previous one can be adopted also to this phenomenon.

One more mechanism of a radiative influence the condensation kinetics should be taken into account, for instance, under studying recondensation of water vapor in the cometary coma which occurs in the presence of the Solar light giving rise to radiative excitation of the rovibrational sublevels of the water molecule. This processes is investigated in [12]. Two main assumptions are made when treating the mechanism of the coupled radiation and condensation. First, the excitation of the vibrational states of the water molecule is assumed to be inefficient due to low temperatures on the surface of the cometary nucleus $T = 100-200K$. However, such an assumption is not a restriction of our microscopic

theory because in its original version the intramolecular vibrations are taken into account and therefore this case is only the simplification of the problem with allowance for the real physical picture. Secondly, we suppose that the rotationally-excited molecule has a less cross-section of condensation as compared with unexcited one. This problem has been theoretically explored in [13] aimed to explain experiments on the rotationally-selective condensation of water and heavy water molecules [14]. The mechanism of the resonance association of molecules via the formation of an intermediate complex was considered and illustrated for the He – H_2O system. Based upon the estimations of this work ratio η of the dimerization rate constants of water molecules being in the ground ortho and para states was found to be $8.4 \leq \eta \leq 12.3$ on the temperature range $30K \leq T \leq 50K$. Thus, this data gives an evidence of the possibility of the rotationally-selective mechanism of condensation even on the stage of dimerization. It is clear that the rate of dimerization decreases with the increase of the rotational energy of the molecule. That is why in [12] we use a model where the only molecules being in the ground rotational para-state are efficient to be attached to the cluster while the possibility of condensation of the other molecules is left aside. It turns out that under the assumptions made a natural enhancement of our microscopic theory is possible. However, nonequilibrium redistribution of energy over the rotational levels strongly influence the condensation kinetics. In particular, the final equation for S is similar in its structure to (1), but its rhp depends upon the population of the ground rotational para-state in a more complicated way.

Acknowledgments

This work was supported by the Russian Ministry of Science and Technical Policy and Russian Foundation of Basis Researches (grant N 95-01-01480). The author thanks Dr. E.G. Kolesnichenko for fruitful discussions.

References

[1] Itkin AL and Kolesnichenko EG. On the kinetic mechanism of photonucleation. *Chemical Physics*, 1994, 11(12): 2382–2400.

[2] Wen F, McLaughlin T and Katz J. Photoinduced nucleation of water vapor. *Science*, 1978, 200: 769–771.

[3] Bogdanov AV, Itkin AL and Kolesnichenko EG. The transport processes inside a thermal diffusion chamber under a photoinitiated condensation. *Fluid Dynamics*, 1991, 26(6): 870–878.

[4] Chen C and Katz J. Condensation of supersaturated vapor. vii. the photoinduced nucleation of o-tolualdehyde and its underlying reaction mechanism. *J. Chem. Phys.*, 1988, 88: 5007–5013.

[5] Bogdanov AV, Itkin AL et al. Analytical investigation of equilibrium and steady-state solutions for a quasichemical condensation model. *Soviet J. Chem. Phys.*, 1992, 9(5): 1113–1129.

[6] Cordier B, Papon P and Leblond L. Photonucleation in supersaturated ccl_4 vapor investigated in a diffusion chamber. *J.Chem.Phys.*, 1981, 74: 3353–83361.

[7] Gertler A, Berg J and El-Sayed M. On the mechanism of photounduced nucleation in a diffusion cloud chamber. *Chem. Phys. Lett.*, 1978, 57: 343–347.

[8] Katz J, Wen F et al. Nucleation on photoexcited molecules. *Science*, 1977, 196: 1203–1205.

[9] Beterov IM, Brzhazovskii YV et al. *Letters in Soviet J. Techn. Phys.*, 1978, 4: 1446–1449.

[10] Itkin AL and Kolesnichenko EG. Microscopic theory of condensation in gases and plasma. Singapoure: World Scientific, 1996, *in press.*

[11] Wen F, McLaughlin T and Katz J. Photoinduced nucleation of supersaturated vapors in the presence of carbon disulfide. *Phys. Rev. A*, 1982, A26: 2235–2242.

[12] Itkin AL, Kolesnichenko EG and Bockelee-Morvan D. Nonequilibrium processes and their effect on the struc of the inner coma of comets. III. Effect of coupled radiatiave excitation and recondensation of water vapor. *Researches*, 1996, *in press.*

[13] Epifanov SY and Phayzulaev VN. Multistep model of the capture under the molecular association in gases. *Pre Inst.Gen.Phys. RAS*, 1992. **4**.

[14] Konuhov VK, Prohorov AM et al. Rotationally-selected condensation and a separation of spin-modificatio water and heavy water. *Izv.AS SSSR*, 1988. 52: 1059–1065.