Supporting Information: Probing Methanol Cluster Growth by Vacuum Ultraviolet Ionization

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Characterization of the supersonic expansion

We have used high mach number flow set up as implemented in Molecular Flow module in the COMSOL multiphysics software package. We have assumed that the flow is compressible which satisfies the Navier-Stokes (N-S) equation, the continuity, and the energy conversion equation.

$\frac{\delta\rho}{\delta t} = \nabla.(\rho v) = 0$

$\frac{\delta}{\delta t}(\rho v) + \nabla.(\rho vv + pI - \tau) = \rho f$

$\frac{\delta}{\delta t}(\rho E) + \nabla[\rho v(E + \frac{p}{\rho}) + q - \tau.v] = \rho f.v$

where, v is velocity vector, $E = p/(\rho(\gamma - 1) + v^2/2$ is the total energy, τ is a second order tensor representing the viscous stresses with elements. We assumed a perfect gas which obeys the ideal gas equation $p = \rho RT$ where p is the static pressure, ρ is the gas density, T is the temperature, and R is the gas constant. We also assumed that the flow to be laminar, adiabatic and axisymmetric; the chamber walls are thermally insulated with no slip conditions. The boundary conditions are given below:

inlet: 101,325 Pa; T=300 K, M=0.05, u=10 m/s

outlet: 12,666 Pa;

fluid is argon.

We have used different meshes, different inlet/outlet pressure ratios. We have shown only one pressure ratio in the paper.

Thomson's equation[2,3]

$$\triangle G_n = -nk_BTln(S) + 4\pi r_n^2\sigma + \frac{q^2}{8\pi\epsilon_0}(1-\frac{1}{\epsilon})(\frac{1}{r_n}-\frac{1}{r_i}) \quad (1)$$

$$r_n = n^{\frac{1}{3}}(\frac{3M}{4\pi\rho N})^{\frac{1}{3}} \quad (2)$$

Where,

$\triangle G_n$	Free energy change for $n-th$ molecule	$kJmol^{-1}$
n	number of molecules	
k_B	Boltzmann Constant	$1.38 \times 10^{-23} m^2 kgs^{-2} K^{-1}$
T	Temperature	276 K
S	Supersaturation ratio	
σ	Surface tension of methanol at 276 K	24.01 mNm^{-1}
r_n	Radius of the cluster with n numbers of molecule	m
r_i	Radius of the nucleating methanol ion	2.7×10^{-10} m
q	Charge	C
ϵ	vacuum permittivity	8.854×10^{-12} Fm^{-1}
ϵ_r	Dielectric constant of methanol	32.7
M	Molecular weight	32.04 $gmol^{-1}$
ρ	Density	791.8 kgm^{-3}
N	Avogadro's number	6.023×10^{23}

Kinetic and Thermodynamic Equivalence[4]

Ion molecule reactions can be considered as analogous to Lindeman type mechanism: $M^+ + L + A \rightleftharpoons M^+L + A$, and $ML^+ + L + A \rightleftharpoons M^+L_2 + A$ ..., and so on. Here A is a third body required for the collision and remains unchanged after the reaction. The cluster formation kinetics can then be written in terms of rate constants of the individual association reaction:

$$M^+L_{n-1} + L \underset{k_{r,n}}{\overset{k_{f,n-1}}{\rightleftharpoons}} M^+L_n \tag{3}$$

$$M^+L_{n^*} + L \overset{k_{n^*}}{\rightarrow} M^+L_{n^*+1} \tag{4}$$

Where k_f and k_r are the rate of forward and backward rate of the reaction (3). The overall rate of particle formation is dependent on the critical cluster (n^*) formation and can be written as pseudo second order rate constants:

$$Rate = k_{n^*}[L]_{n^*+1}\prod_{n=1}^{n^*}K_{n-1,n} \tag{5}$$

Where $K_{n-1,n}$ is the equilibrium constant of the reaction (3) and for an equilibrium system, $\Delta G_{n-1,n} = -Nk_bTln(K_{n-1,n})$. Substitution of $K_{n-1,n}$ to equation (5) leads to:

$$Rate = k_n * [L] * exp\left(-\sum_{n=1}^{n^*}\Delta G_{n-1,n}/Nk_bT\right) \tag{6}$$

Here, it should be noted that the rate expression is obtained assuming the equivalence between equilibrium and the steady state. This also assumes that after the critical cluster formation the reaction proceeds only in the forward direction. In the case of finite nucleation

rates, equilibrium values of cluster concentrations will be different from those of the steady state. The correspondence between the kinetic model and energy barrier in the classical model is realized by equation 6; it is evident that ($\triangle G_{c,ion}$) in Thomson's model and ($\Delta G_{n-1,n}$) in equation 6 is identical if steady state is assumed to be equivalent to equilibrium.

References

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Table 1: Appearance Energies (A. E.) for pure methanol and protonated methanol clusters evaluated from PIE curves. A. E. values have uncertainties of ±0.1 eV.

	Appearance energies (AE), eV				
Ion	MS-Ionization[1]	$x = 2\ mm$	$x = 15\ mm$	$x = 20\ mm$	$x = 25\ mm$
CH_3OH^+	10.8	10.8	10.8	10.8	10.8
$H^+(CH_3OH)$	10.2	10.1	10.2	10.3	10.3
$H^+(CH_3OH)_2$	10.1	9.9	10.0	9.8	9.9
$H^+(CH_3OH)_3$	9.8	9.5	9.6	9.7	9.7