



## Investigation of Formic Acid involved Molecular Clusters with Atmospheric Acidic, Basic and Neutral Species

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New particle formation (NPF) is regarded as a main source of tropospheric aerosols. Formic acid (FA) is investigated as a source of NPF by studying its dimer, trimer and tetramer clusters with atmospheric nucleating species like H<sub>2</sub>O, H<sub>2</sub>S, MeNH<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> employing quantum chemical methods. The structural characteristics, nature of interactions, interaction energies, harmonic vibrational frequencies, thermochemistry at ambient and tropospheric conditions are investigated employing DFT and MP2 methods. Acidic (H<sub>2</sub>S), basic (MeNH<sub>2</sub>) and neutral (H<sub>2</sub>O) nucleating precursors are chosen to study the effect of nature of these species on NPF. Results show that clusters of formic acid with MeNH<sub>2</sub> have more stabilising effect than clusters with H<sub>2</sub>O, H<sub>2</sub>S and H<sub>2</sub>O<sub>2</sub>. The FA-MeNH<sub>2</sub> clusters are formed spontaneously at ambient conditions while for others (H<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub>) although the clusters are stable at ambient conditions, yet have positive binding free energy that becomes negative at tropospheric conditions. The cluster formation leads to significant red shifts and increased IR intensities for conventional hydrogen bond donor bond stretching vibrations relative to its monomeric units. For all the nucleating species, stability increases with the growth of clusters.

**Keywords:** Cluster, Nucleation, Dimer, Binding energy, Hydrogen bonding.

### INTRODUCTION

The harmful effect of pollutants is a matter of intense public and scientific concern due to their detrimental effects on plants, animals and human life [1]. Various organic and inorganic pollutants adversely affect environment causing photochemical air pollution, changes in ozone layer, acid deposition, global climate change, *etc.* [2-4]. In recent decades, the interest in role of organic acid pollutants as chemical constituents of troposphere has significantly enhanced. Observations of atmospheric aerosols have revealed the presence of organic carbonyls and acids, which may contribute to nanoparticle nucleation and growth [5,6]. The organic acids contribute significantly to the atmospheric aqueous phase chemistry, acidity of precipitation and aerosol formation [7,8]. Formic acid (FA) is the simplest and the dominant organic acid, found in atmospheric gases, aerosols and droplets [9]. It is reported to be present in particulate matter with concentration ranging between 0-7 ppbV. On an average nearly 53% of formic acid and 67% of

the acetic acid are present in particulate matter and recent studies suggest acidity is main characteristic of PM<sub>2.5</sub> [10]. Although the atmospheric sources of formic acid are ambiguous yet most likely suggested predominant sources of formic acid include photochemical oxidation of biogenic and anthropogenic volatile organic compounds (*e.g.*, isoprene oxidation) [11], combustion of fossil fuels [12], forest fires, acetaldehyde tautomerization [11], stabilized Criegee intermediates (SCIs) [11], organic aerosol aging in laboratory, reaction of hydrated formaldehyde with OH of cloud water, reaction of olefins with ozone, reaction of peroxyacetyl radical CH<sub>3</sub>-CO (OO) with hydroperoxyl (HOO) [1], methyl peroxy (CH<sub>3</sub>OO) or other primary and secondary radicals, vehicular emissions, natural sources like the ants [13], plants [14], effusions from soil [15], direct and secondary emission from vegetation [16]. Formic acid facilitates nucleation of cloud droplets contributing to acidity of clouds. Formate and acetate together contribute more than 60% of free acidity of rain in remote regions [1]. Major health effects associated with formic acid exposure include

respiratory illness, neurologic, dermatological, cardiovascular effects, *etc.* [17]. Formic acid has an overall atmospheric lifetime of 2-4 days; however it can be as long as 25 days in cloud-less tropospheric conditions [8,16,18]. A study by Jacob *et al.* [19] suggested that the formic acid can survive in upper troposphere for several weeks. The clouds are suggested to be a probable sink for atmospheric formic acid [20]. Another minor sink is irreversible deposition on dust [16,21].

New particle formation (NPF) occurs in atmosphere when certain ingredients clump together spontaneously, causing the formation of new particles [22]. It is reported to contribute largely to the global aerosol formation [23]. The ultrafine particles pose problems for air quality and threat to our health. Long term exposure to ultrafine particles causes inflamed lungs, leading to lung cancer and cardiovascular diseases [24]. World health organization has estimated 4.2 million deaths annually linked to air pollution [25]. The detailed and comprehensive understanding of initial steps in the growth of newly formed particles into bigger size is of huge interest to researchers in order to acquire deeper understanding of global climate system and enhance control the adverse health effect of ultrafine aerosol particles.

In order to better understand new particle formation, their growth at molecular level, nucleation and the effect of neutral, acidic, basic species on new particle formation (NPF), the investigation of structural characteristics and thermodynamics of gas phase clusters of formic acid with H<sub>2</sub>O (neutral species), H<sub>2</sub>S (acidic species), H<sub>2</sub>O<sub>2</sub>, MeNH<sub>2</sub> (basic species) is carried out as model systems employing quantum chemical methods.

## COMPUTATIONAL METHODS

The geometry optimization and harmonic vibrational frequencies of various possible formic acid containing clusters have been performed employing Becke-3-parameter, exchange density functional theory (DFT) with non-local hybrid correlation given by Lee-Yang and Parr as instigated in Gaussian 03

software in conjunction with Dunning's correlation consistent basis set aug-cc-pVDZ on all conformers [26]. All the optimized structures were confirmed to be global minima by computing harmonic vibrational frequencies. The binding energies are calculated by taking difference in energy of each aggregate and sum of isolated monomer. The binding energies were corrected with zero-point vibrational energies (ZPEs). For correcting binding energies the basis set superposition error (BSSE) is also calculated using counterpoise (CP) method [27]. A number of research groups have employed DFT methods along with Dunning's pvdz basis set for the study of atmospheric clusters because of excellent performance of the theoretical level as evidenced from closeness of binding energies with experimental data [28-30]. Natural bond orbital (NBO) analysis [31] was applied for investigating donor-acceptor interactions and 2<sup>nd</sup> order interaction energies  $E^{(2)}$  values in the complexes of formic acid with H<sub>2</sub>O, H<sub>2</sub>S, H<sub>2</sub>O<sub>2</sub> and MeNH<sub>2</sub>. Atomic charges have been determined using natural population analysis (NPA) method incorporated within NBO.

## RESULTS AND DISCUSSION

Formic acid (FA) is an important atmospheric ligand with pKa 3.75 [32]. It is very interesting to investigate contribution of formic acid containing clusters to new particle formation (NPF). Hence, the interactions of simplest organic acid (FA) have been studied with common atmospheric nucleation precursors (H<sub>2</sub>O, H<sub>2</sub>S, MeNH<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>) employing computational methods. The study will give deeper insights into how the acidic, basic and neutral character of these nucleating species affects the NPF. The optimized geometries of all the dimeric clusters of nucleating species among themselves along with FA containing bimolecular clusters optimized at B3LYP/AUG-cc-PVDZ level are presented in Figs. 1 and 2, respectively. All the optimized clusters are stabilized by hydrogen bonding. The presence of X-H...Y hydrogen bonds in the complexes has been explored by analyzing the geometrical features like

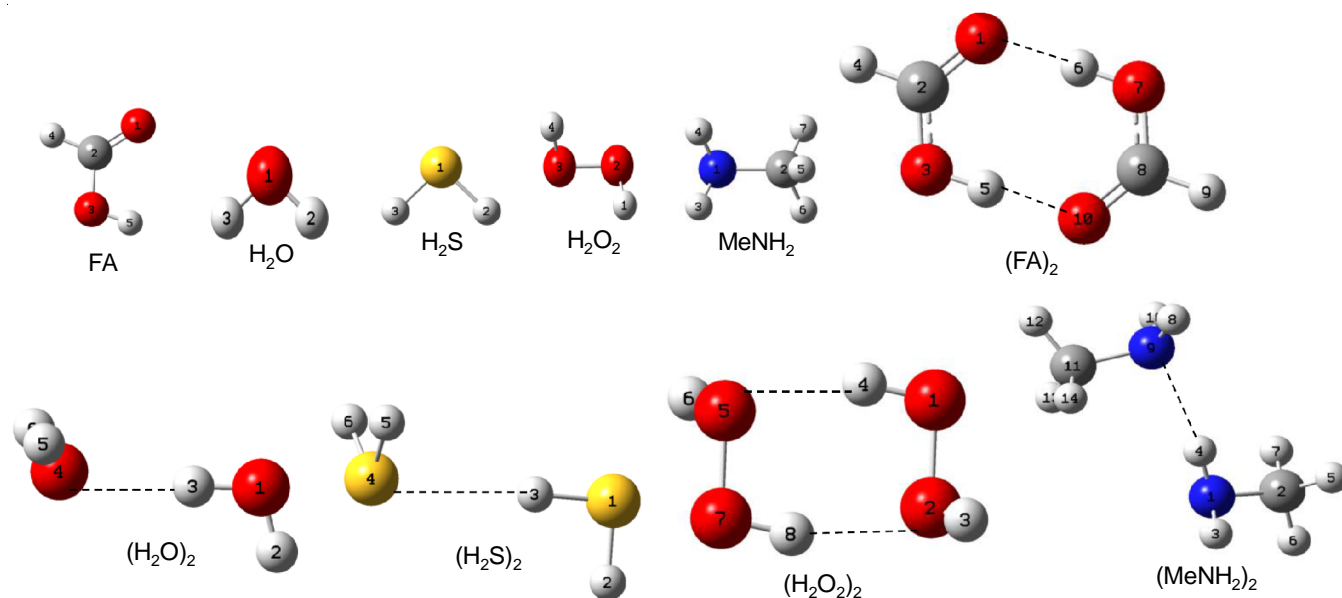
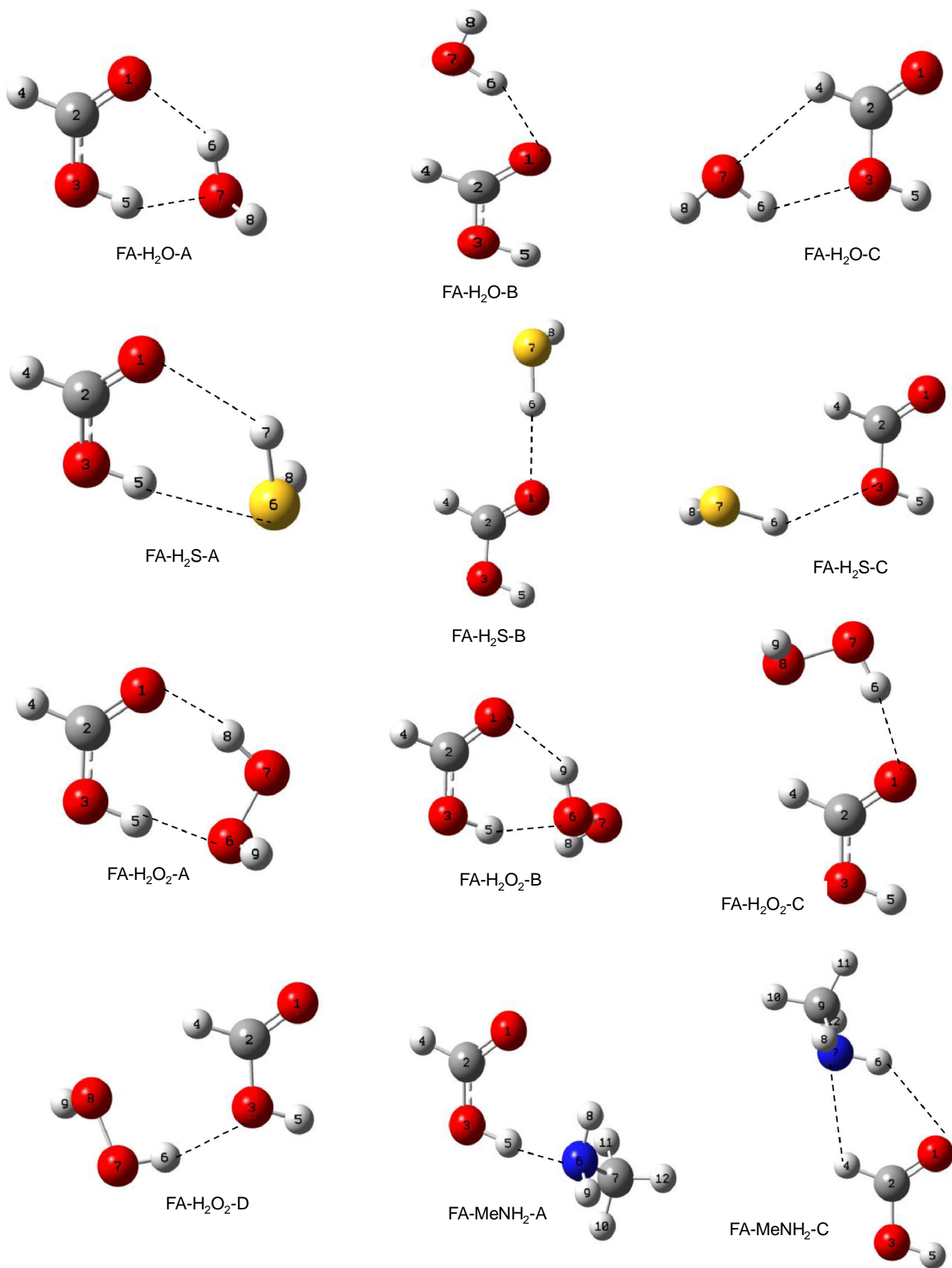


Fig. 1. Monomer and dimer structures optimized at B3LYP/Aug-cc-pVDZ Level

Fig. 2. Dimer structures of FA with H<sub>2</sub>O, H<sub>2</sub>S, H<sub>2</sub>O<sub>2</sub> and MeNH<sub>2</sub> optimized at B3LYP/aug-cc-pVDZ level

important hydrogen bonding parameters (non-bonded distances of hydrogen bond (HB) donor and acceptor, angle at bridging hydrogen), calculated interaction energies *i.e.* binding energies, zero point vibrational energy, counterpoise corrected stabilization energies and BSSE calculated at 298.15 K and 1 atm pressure employing B3LYP/aug-cc-pVDZ (L1) level (Table-1). The optimized structures were used to perform single point energy calculation at MP2/aug-cc-pVDZ//B3LYP/aug-cc-pVDZ (L2) theoretical level. It is widely accepted that the shorter the H...Y distance is and the closer the angle X-H...Y is to 180°, the stronger the hydrogen bonding is. It is found that a number of optimized clusters have very short, near linear hydrogen bonds. Meanwhile, the zero point energies (ZPEs) for 1:1 complexes range from 0.77-2.52 kcal/mol for studied systems. The small value of BSSE in all the clusters can be assigned to elimination of BSSE by usage of the large basis set like aug-cc-pVDZ. Thus for most dimers, the B.E. at L1 level are very close to CP corrected S.E. The B.E. obtained at L2 are little larger than B.E. at L1 level. The B.E. obtained at L2 is used for discussion unless mentioned. Table-1 data indicated that B.E. calculated for dimeric cluster namely (MeNH<sub>2</sub>)<sub>2</sub>, (H<sub>2</sub>O)<sub>2</sub>, (H<sub>2</sub>S)<sub>2</sub>, (H<sub>2</sub>O)<sub>2</sub> is less than (FA)<sub>2</sub>.

**FA-H<sub>2</sub>O dimeric clusters:** The concentration of water in atmospheric vapour ranges from 10 to 50,000 ppmV [33]. The strong hydrogen bonding (HB) interactions of atmospheric water vapours with radicals and other molecules can result in NPF, from which atmospheric aerosols originate. Formic acid has OH group and C=O, O-H is good HB donor and O atom of C=O is good HB acceptor. Three hydrogen bonded com-

plexes namely FA-H<sub>2</sub>O-A, FA-H<sub>2</sub>O-B, FA-H<sub>2</sub>O-C with H<sub>2</sub>O are optimized at B3LYP/aug-cc-pVDZ (L1) theoretical level. The FA-H<sub>2</sub>O-A is most stable with B.E. of -10.51 kcal/mol at L2 level. Nevertheless the other dimer clusters FA-H<sub>2</sub>O-B (B.E. = -5.70 kcal/mol) and FA-H<sub>2</sub>O-C (-4.01 kcal/mol) with one HB are much less stable than corresponding cyclic cluster FA-H<sub>2</sub>O-A. FA-H<sub>2</sub>O-A cyclic structure is formed by two hydrogen bonds C=O...H-O and O-H...O. Table-2 displays the change in HB donor ( $\Delta d$  in Å) on complexation. Upon complexation the O-H of formic acid in FA-H<sub>2</sub>O-A is elongated by 0.20 Å as compared to isolated monomer. The electron rich oxygen atom of water and hydrogen atom of formic acid form strong HB of length 1.773 Å. Our calculated counterpoise corrected B.E. for this structure is -9.81 kcal/mol, which is in good agreement with earlier reported value of -9.15 kcal/mol at B3LYP/6-311++G (2d,2p) [34]. The interaction energy of the (H<sub>2</sub>O)<sub>2</sub> dimer was calculated to be -5.26 kcal/mol at L2 level. The experimental value of B.E. of water dimer is -5.4 ± 0.7 kcal/mol [35]. The FA-H<sub>2</sub>O-A and FA-H<sub>2</sub>O-B dimer complexes are more stable in interaction energies (binding energies -10.51 and -5.70 kcal/mol) than (H<sub>2</sub>O)<sub>2</sub> dimer (-5.26 kcal/mol). The B.E. of C<sub>2</sub>h symmetrical (FA)<sub>2</sub> at L2 level is -16.44 kcal/mol. Counterpoise corrected B.E. of (FA)<sub>2</sub> is 18.22 kcal/mol, which agrees well to the previous reported value of 18.75 kcal/mol [36]. Energetic analysis shows that formic acid prefers to form dimer with itself than with H<sub>2</sub>O as is evidenced from larger B.E. in former case than latter.

In the troposphere, new particle formation occurs between 0-12 km altitude. Temperature has a significant impact on

TABLE-1  
IMPORTANT HYDROGEN BONDING PARAMETERS, HYDROGEN BOND DISTANCES, HYDROGEN BOND ANGLES CALCULATED BINDING ENERGY (BE), ZERO-POINT VIBRATIONAL ENERGY (ZPE), FOR THE DIMER COMPLEXES (298 K AND 1 atm) AT B3LYP/aug-cc-pVDZ (L1) AND AT THE MP2/aug-cc-pVDZ//B3LYP/aug-cc-pVDZ (L2) THEORETICAL LEVEL

Conformer	Hydrogen bonded distances (Å)	Hydrogen bonded angles (°)	B.E. (L1)	ZPVE (L1)	CP corrected B.E.	BSSE	B.E. (L2)
(H <sub>2</sub> O) <sub>2</sub>	O4...H3 1.943	O4...H3-O1 173.7	-4.70	2.10	-4.51	0.23	-5.26
(H <sub>2</sub> S) <sub>2</sub>	S4...H3 2.871	S4...H3-S1 178.8	-1.15	1.05	-1.00	0.16	-2.28
(MeNH <sub>2</sub> ) <sub>2</sub>	N9...H4 2.263	N9...H4-N1 166.3	-2.91	1.03	-2.82	0.13	-4.50
(H <sub>2</sub> O) <sub>2</sub>	O5...H4 1.915	O5...H4-O1 156.6	-7.79	2.22	-7.47	0.47	-9.72
	O2...H8 1.915	O2...H8-O7 156.6					
(FA) <sub>2</sub>	O1...H6 1.658	O1...H6-O7 179.1	-15.72	1.86	-18.22	0.67	-16.44
	O10...H5 1.658	O10...H5-O3 179.1					
FA-H <sub>2</sub> O-A	O1...H6 2.002	O1...H6-O7 136.8	-9.61	2.52	-9.81	0.45	-10.51
	O7...H5 1.773	H5...O7-H6 156.6					
FA-H <sub>2</sub> O-B	O1...H6 1.991	O1...H6-O7 149.4	-4.79	1.79	-4.39	0.52	-5.70
FA-H <sub>2</sub> O-C	O3...H6 2.221	O3...H6-O7 130.9	-2.76	1.34	-2.39	0.45	-4.01
	O7...H4 2.557	O7...H4-C2 118.5					
FA-H <sub>2</sub> S-A	O1...H7 2.570	O1...H7-S6 127.2	-4.39	1.36	-4.31	0.24	-6.03
	S6...H5 2.403	S6...H5-O3 168.9					
FA-H <sub>2</sub> S-B	O1...H6 2.228	O1...H6-S7 177.6	-2.00	0.96	-1.81	0.21	-3.12
FA-H <sub>2</sub> S-C	O3...H6 2.525	O3...H6-S7 146.8	-0.95	0.77	-0.79	0.17	-2.34
FA-H <sub>2</sub> O <sub>2</sub> -A	O1...H8 1.795	O1...H8-O7 165.5	-11.39	1.67	-11.70	0.56	-12.90
	O6...H5 1.762	O6...H5-O3 171.0					
FA-H <sub>2</sub> O <sub>2</sub> -B	O1...H9 1.982	O1...H9-O6 135.6	-7.31	2.24	-7.29	0.49	-8.58
	O6...H5 1.870	O6...H5-O3 153.8					
FA-H <sub>2</sub> O <sub>2</sub> -C	O1...H6 1.879	O1...H6-O7 164.5	-6.35	1.50	-5.99	0.46	-7.72
FA-H <sub>2</sub> O <sub>2</sub> -D	O3...H6 2.015	O3...H6-O7 160.1	-3.61	1.13	-3.34	0.40	-5.39
FA-MeNH <sub>2</sub> -A	H5...N6 1.691	N6...H5-O3 171.3	-11.94	1.55	-13.01	0.42	-13.62
FA-MeNH <sub>2</sub> -B	O1...H6 2.451	O1...H6-N7 133.7	-3.13	0.98	-2.94	0.19	-4.68
	N7...H4 2.590	N7...H4-C2 117.1					



TABLE-2  
THE VIBRATIONAL FREQUENCIES (cm<sup>-1</sup>), IR INTENSITIES (KM/mol), The Change In Vibrational Frequencies ( $\Delta V$ ) AND CHANGE IN BOND LENGTHS ( $\Delta d$ ) OF BONDS OF CLUSTERS INVOLVED IN HYDROGEN BONDING CALCULATED AT L1 LEVEL

Species	Bond	Fre- quency	Intensity	$\Delta V$	$\Delta d$	Species	Bond	Fre- quency	Intensity	$\Delta V$	$\Delta d$
(H <sub>2</sub> O) <sub>2</sub>	O1-H3	3673.7	337.7	-122.7	0.008	FA-2H <sub>2</sub> S	C2=O1	1772.1	395.2	-32.63	0.007
(H <sub>2</sub> S) <sub>2</sub>	S1-H3	2626.0	73.6	-44.5	0.004		O3-H5	3409.7	827.6	-307.57	0.015
(MeNH <sub>2</sub> ) <sub>2</sub>	N1-H4	3428.9	147.0	-62.3	0.005		S10-H9	2624.9	125.6	-45.52	0.006
(H <sub>2</sub> O) <sub>2</sub>	O1-H4	3575.9	677.7	-176.8	0.011		S6-H7	2542.5	246.8	-128.01	0.011
	H8-O7	3536.6	0.004	-216.8	0.011	2FA-H <sub>2</sub> S	C2=O1	1745.6	180.1	-59.1	0.011
FA-H <sub>2</sub> O-A	O7-H6	3623.1	271.9	-173.3	0.012		O3-H5	3279.5	1052.2	-437.7	0.022
	O3-H5	3316.0	600.9	-401.2	0.020		S6-H7	2546.6	353.9	-123.9	0.012
	C2=O1	1759.5	329.5	-45.2	0.013		C10=O9	1776.1	769.5	-28.5	0.011
FA-H <sub>2</sub> O-B	O7-H6	3689.5	271.9	-106.9	0.007		O11-H13	3467.3	921.2	-249.9	0.013
	C2=O1	1779.6	371.1	-25.1	0.006	2FA-2H <sub>2</sub> S	C2=O1	1766.0	55.3	-38.7	0.008
FA-H <sub>2</sub> O-C	O7-H6	3774.9	31.4	-21.6	0.002		S14-H15	2617.2	280.4	-53.3	0.006
	C2-H4	3093.3	9.4	28.2	-0.002		H13-O11	3355.9	551.5	-361.3	0.018
FA-H <sub>2</sub> S-A	C2=O1	1779.2	310.6	-25.5	0.005		C10=O9	1771.6	913.8	-33.1	0.008
	O3-H5	3475.0	652.1	-242.2	0.011		S6-H7	2606.3	133.1	-64.3	0.007
	S6-H7	2645.6	12.0	-24.9	0.003	FA-2MeNH <sub>2</sub>	O3-H5	3373.4	1372.8	-343.8	0.017
FA-H <sub>2</sub> S-B	C2=O1	1790.3	480.9	-14.4	0.003		O3-H5	2382.6	2545.4	-1334.7	0.072
	S7-H6	2625.8	122.5	-44.7	0.005		N6-H7	3265.6	457.3	-225.6	0.015
FA-H <sub>2</sub> S-C	S7-H6	2665.5	6.6	-4.9	0.001		C2=O1	1722.9	525.4	-81.7	0.016
FA-H <sub>2</sub> O <sub>2</sub> -A	C2=O1	1749.2	344.7	-55.5	0.014		N13-H14	3441.8	147.8	-49.5	0.005
	O3-H5	3285.6	326.1	-431.6	0.021	2FA-MeNH <sub>2</sub>	O3-H5	2003.4	2547.8	-1713.8	0.100
	O7-H8	3418.7	1027.9	-334.7	0.008		N11-H17	3388.9	446.3	-102.4	0.009
FA-H <sub>2</sub> O <sub>2</sub> -B	C2=O1	1764.4	349.3	-40.3	0.011		O8-H10	3282.4	1139.6	-434.9	0.022
	O6-H9	3582.0	377.9	-171.4	0.011		C2=O1	1644.4	516.6	-160.3	0.023
	O3-H5	3438.1	410.3	-279.2	0.014		C7=O6	1758.5	783.6	-46.2	0.014
FA-H <sub>2</sub> O <sub>2</sub> -C	C2=O1	1769.3	409.2	-35.4	0.008	2FA-2MeNH <sub>2</sub>	C2=O1	1716.9	1179.1	-87.7	0.020
	O7-H6	3553.7	512.9	-199.7	0.011		O3-H5	2209.4	3961.8	-1507.8	0.085
FA-H <sub>2</sub> O <sub>2</sub> -D	O7-H6	3671.7	274.3	-81.7	0.005		N11-H23	3425.0	434.9	-66.2	0.007
FA-MeNH <sub>2</sub> -A	O3-H5	2786.6	2058.2	-930.7	0.047		C7=O6	1682.4	0.8	-122.3	0.020
FA-MeNH <sub>2</sub> -B	C2-H4	3083.2	10.9	+18.05	-0.002		O8-H10	2180.9	1294.8	-1536.3	0.085
	C2=O1	1780.2	336.9	-24.47	0.005	FA-2H <sub>2</sub> O <sub>2</sub>	N14-H24	3420.9	61.8	-70.3	0.007
	H6-N7	3478.0	12.8	-13.22	0.002		C2=O1	1740.7	475.1	-63.9	0.017
FA-2H <sub>2</sub> O	C2=O1	1742.1	410.9	-62.62	0.017		O3-H5	3153.6	711.5	-563.6	0.028
	H10-O9	3518.9	805.8	-277.55	0.017		O6-H9	3333.2	968.0	-420.2	0.023
	H8-O6	3383.5	701.9	-412.96	0.023	2FA-H <sub>2</sub> O <sub>2</sub>	H11-O10	3402.6	1123.5	-350.7	0.021
	H5-O3	3029.2	1215.2	-688.01	0.035		C2=O1	1717.1	160.5	-87.6	0.018
2FA-H <sub>2</sub> O	C2=O1	1720.6	134.4	-84.10	0.018		O3-H5	3086.1	196.8	-631.2	0.032
	C10=O9	1762.4	843.3	-42.32	0.016		O6-H7	3318.8	1935.6	-434.6	0.025
	O11-H13	3297.5	1176.0	-498.93	0.022		C11-O10	1760.8	869.7	-43.9	0.017
	O3-H5	2975.7	1402.6	-741.52	0.038	2FA-2H <sub>2</sub> O <sub>2</sub>	O12-H14	3278.8		-474.6	0.022
	O6-H7	3446.6	1102.4	-349.87	0.020		O3-H5	3321.1	494.9	-396.1	0.020
2FA-2H <sub>2</sub> O <sub>2</sub>	C2=O1	1753.3	617.1	-51.36	0.014		C2=O1	1754.7	669.5	-50.0	0.013
	C10=O9	1716.9	234.4	-87.73	0.022		H16-O15	3428.8	1001.4	-324.6	0.017
	O3-H5	3175.2	1321.5	-542.09	0.027		H14-O12	3050.5	640.9	-666.8	0.033
	H15-O14	3541.7	672.1	-254.72	0.016		C11=O10	1719.7	256.3	-85.0	0.021
	O11-H13	2843.3	1570.6	-953.1	0.046		O6-H7	3161.7	256.3	-591.7	0.032
	O6-H7	3333.8	964.6	-462.67	0.027		O17-H18	3592.7	302.5	-160.7	0.009
	O14-H16	3760.2	149.9	-36.20	0.005						

particle binding energy. For every 1 km of altitude, the temperature decreases by 6.49 K and at 12 km (troposphere) it reaches 216.69 K. The study of thermochemical data is essential to explore mechanism of atmospheric nucleation. Effect of decrease in temperature on NPF was studied by calculating binding free energy of dimer, trimer and tetramer at B3LYP level in conjunction with aug-cc-pVDZ basis set at 12 km (216.69 K). Thermochemical properties like binding free energy and enthalpy of clusters are calculated at two temperatures *i.e.* at 298 K and 216.69 K and are listed in Table-3. Inspection of thermochemical data illustrates that dimer, trimer and tetramer cluster formation is exothermic process at all studied conditions. The

$\Delta H$  values decreases with increased atmospheric height but  $\Delta G$  values show that not all the processes are spontaneous at 298 K.

At ambient situation, the Gibbs free energies of formation of FA-H<sub>2</sub>O dimer range from 1.79 to 5.69 kcal/mol. The B.E. indicate that interaction between water and formic acid is very strong, yet Gibbs free energies of formation indicate that studied systems are not thermodynamically stable at ambient conditions.

**FA-H<sub>2</sub>S dimeric clusters:** H<sub>2</sub>S is an environment hazard with concentrations in ambient conditions reported to range from 0.11-0.33 ppb [37]. Interaction of formic acid with H<sub>2</sub>S

TABLE-3  
CALCULATED BINDING FREE ENERGY ( $\Delta G^{298.15}$ ,  $\Delta G^{216.69}$ ) AND ENTHALPIES ( $\Delta H^{298.15}$ ,  $\Delta H^{216.69}$ )  
FOR DIMER, TRIMER AND TETRAMER OF CLUSTERS AT B3LYP/aug-cc-pVDZ

Conformer	T = 298.15 K, P = 1 Atm		T = 216.69, P = 10000 Millibar		Conformer	T = 298.15 K, P = 1 Atm		T = 216.69, P = 10000 Millibar	
	$\Delta G^{298.15}$	$\Delta H^{298.15}$	$\Delta G^{216.69}$	$\Delta H^{216.69}$		$\Delta G^{298.15}$	$\Delta H^{298.15}$	$\Delta G^{216.69}$	$\Delta H^{216.69}$
(FA) <sub>2</sub>	-3.08	-14.27	-6.15	-14.37	FA-MeNH <sub>2</sub> -A	-1.29	-10.49	-3.82	-10.64
(H <sub>2</sub> O) <sub>2</sub>	3.85	-3.08	1.94	-3.22	FA-MeNH <sub>2</sub> -B	5.51	-1.69	3.50	-1.97
(H <sub>2</sub> S) <sub>2</sub>	5.51	0.12	4.00	-0.14	FA-2H <sub>2</sub> O	1.85	-17.65	-3.48	-17.71
(H <sub>2</sub> O) <sub>2</sub>	3.64	-6.08	0.98	-6.18	2FA-H <sub>2</sub> O	-0.76	-20.49	-6.17	-20.70
(MeNH <sub>2</sub> ) <sub>2</sub>	4.87	-1.45	3.11	-1.71	2FA-2H <sub>2</sub> O	2.45	-27.91	-5.86	-28.08
FA-H <sub>2</sub> O-A	1.79	-7.87	-0.85	-7.93	FA-2H <sub>2</sub> S	11.37	-5.36	6.75	-4.49
FA-H <sub>2</sub> O-B	4.41	-3.19	2.31	-3.37	2FA-H <sub>2</sub> S	6.58	-11.67	1.55	-12.05
FA-H <sub>2</sub> O-C	5.69	-1.37	3.73	-1.62	2FA-2H <sub>2</sub> S	12.42	-10.48	6.07	-11.14
FA-H <sub>2</sub> S-A	5.08	-3.07	2.82	-3.29	FA-2H <sub>2</sub> O <sub>2</sub>	2.98	-16.67	-2.42	-16.94
FA-H <sub>2</sub> S-B	4.83	-0.67	3.29	-0.93	2FA-H <sub>2</sub> O <sub>2</sub>	0.13	-20.01	-5.40	-20.31
FA-H <sub>2</sub> S-C	5.72	0.31	4.20	0.01	2FA-2H <sub>2</sub> O <sub>2</sub>	5.06	-26.24	-3.53	-26.63
FA-H <sub>2</sub> O <sub>2</sub> -A	0.92	-9.68	-1.98	-9.76	FA-2MeNH <sub>2</sub>	10.15	-17.11	-3.64	-17.45
FA-H <sub>2</sub> O <sub>2</sub> -B	3.52	-5.75	0.97	-5.92	2FA-MeNH <sub>2</sub>	5.54	-22.70	-8.41	-23.02
FA-H <sub>2</sub> O <sub>2</sub> -C	3.88	-4.67	1.52	-4.88	2FA-2MeNH <sub>2</sub>	9.32	-30.45	-9.18	-30.95
FA-H <sub>2</sub> O <sub>2</sub> -D	5.67	-2.22	3.48	-2.48					

will model acid-acid interaction and optimization resulted in three dimeric complexes. Most stable out of these is FA-H<sub>2</sub>S-A with B.E. of -6.03 kcal/mol at L2 level. The counterpoise corrected B.E. at L1 level is -4.31 kcal/mol. When H<sub>2</sub>S interacts with formic acid, the O-H bond of formic acid undergoes lengthening by 0.011 Å as compared to free formic acid (Table-2). Two hydrogen bonds with length 2.570 Å and 2.403 Å are formed resulting in this cyclic structure. In the shorter HB, the formic acid acts as HB donor, while in second rather longer HB, H<sub>2</sub>S interacts with lone pair of oxygen of formic acid. strong interaction results when O-H of formic acid act as H-bond donor to S of H<sub>2</sub>S but weak van der Waal interaction occur when O of formic acid acts as HB acceptor to S-H of H<sub>2</sub>S.

A comparison of most stable dimeric cluster FA-H<sub>2</sub>O-A and FA-H<sub>2</sub>S-A indicate FA-H<sub>2</sub>O-A with two short strong O-H...O hydrogen bonds is more stable than FA-H<sub>2</sub>S-A. In FA-H<sub>2</sub>S-A, mainly stabilization results from S of H<sub>2</sub>S as H-bond acceptor. The HB donor ability of S-H of H<sub>2</sub>S is very poor as compared to O-H of H<sub>2</sub>O. Positive Gibbs free energy implies that FA-H<sub>2</sub>S clusters are not thermodynamically stable at 298 K. The S-H of H<sub>2</sub>S is poor HB donor as evident from relatively lower S.E. of FA-H<sub>2</sub>S-B and FA-H<sub>2</sub>S-C involving H<sub>2</sub>S as HB donor only. Although weak interactions of formic acid with H<sub>2</sub>S are observed yet it can't be ignored due to its high concentration in atmosphere.

**FA-H<sub>2</sub>O<sub>2</sub> dimeric clusters:** Four dimeric configurations between formic acid and H<sub>2</sub>O<sub>2</sub> have been optimized. The most stable FA-H<sub>2</sub>O<sub>2</sub>-A, is a seven membered cyclic structure with both formic acid and H<sub>2</sub>O<sub>2</sub> acting as HB donor and acceptor respectively, results in two relatively strong HB. A shorter HB of 1.762 Å is formed between oxygen of H<sub>2</sub>O<sub>2</sub> and hydrogen of formic acid, but formic acid also acts as proton acceptor, resulting in second HB, 1.795 Å, with the peroxide proton. The calculated counterpoise corrected B.E. for this complex is -11.70 kcal/mol at L1 level. Upon the interaction of formic acid with H<sub>2</sub>O<sub>2</sub>, structural changes are observed in formic acid. Its O-H bond gets elongated by 0.021 Å. FA-H<sub>2</sub>O<sub>2</sub>-B, a cyclic

six membered dimeric cluster with little longer and less linear HB angles possess lower S.E. of -7.31 kcal/mol. The other two dimeric clusters FA-H<sub>2</sub>O<sub>2</sub>-C and FA-H<sub>2</sub>O<sub>2</sub>-D with single HB involving formic acid as HB acceptor through carbonyl oxygen and hydroxyl oxygen respectively release much less interaction energy relative to FA-H<sub>2</sub>O<sub>2</sub>-A.

**FA-MeNH<sub>2</sub> dimeric clusters:** The global emissions of MeNH<sub>2</sub> in atmosphere are estimated to be 83 ± 26 Gg N a<sup>-1</sup> [38]. Amines are ubiquitous organic bases of aerosols emitted in atmosphere from biomass burning, vegetation emission, industrial emission, ocean emission, vehicular exhaust [39]. Kurten *et al.* [40] evaluated concentration of atmospheric amines to be 1-100 pptv. Previous studies indicated acid-base interactions (such as H<sub>2</sub>SO<sub>4</sub>-ammonia) occur in initial steps of atmospheric new particle formation. MeNH<sub>2</sub> is the simplest amine chosen for the study of acid-base interaction. Optimization of formic acid with MeNH<sub>2</sub> resulted into two dimeric structures labeled as FA-MeNH<sub>2</sub>-A and FA-MeNH<sub>2</sub>-B. The FA-MeNH<sub>2</sub>-A is more stable with B.E. of -13.62 kcal/mol at L2 level. In the most stable dimeric complexes, H<sub>2</sub>O, H<sub>2</sub>S, H<sub>2</sub>O<sub>2</sub> act as H-bond donor and acceptor however in most stable dimeric cluster with methylamine, although MeNH<sub>2</sub> has two N-H groups yet it does not act as H-bond donor to C=O of formic acid. It can be accounted due to inductive effect of methyl group with enhanced basicity of nitrogen so that MeNH<sub>2</sub> mainly acts as HB acceptor/electron donor. In this dimer, the HB of very short length 1.691 Å and near linear HB angle (171.3°) is formed between nitrogen atom of MeNH<sub>2</sub> and hydrogen atom of formic acid. The  $\Delta d$  value for O-H bond of formic acid in this dimeric cluster is largest *i.e.* 0.047 Å. The other dimer FA-MeNH<sub>2</sub>-B with two weak and bent hydrogen bonds formed by MeNH<sub>2</sub> with formic acid results in nearly one third B.E. of the value obtained for FA-MeNH<sub>2</sub>-A. Compared with acid-acid interaction (FA-H<sub>2</sub>S) and acid-water (FA-H<sub>2</sub>O) interaction, the most favoured interactions are obtained with FA-MeNH<sub>2</sub>. The order of stability of dimeric clusters is MeNH<sub>2</sub> > H<sub>2</sub>O<sub>2</sub> > H<sub>2</sub>O > H<sub>2</sub>S. The interactions

between formic acid and  $\text{MeNH}_2$  are also thermodynamically favoured at 298 K ( $\Delta G = -1.29$ ). For atmospheric  $\text{C}_2\text{H}_2\text{O}_4$ - $\text{MeNH}_2$  interaction, Gibbs free energy of formation was obtained to be  $-7.52$  kcal/mol at PW91PW91/6-311++G (3df,3pd) level [41].

**Growth:** Although molecular clusters grow into larger size forming new aerosol particles yet formation and growth

of small clusters into aerosol particles is largely uncertain. This work concentrates on growth of  $\text{FA-H}_2\text{O}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{MeNH}_2$  clusters. In this study, growth pathway is considered by inserting new nucleating precursor into dimeric cluster. Besides dimeric cluster of formic acid and selected molecules in 1:1 ratio, the trimeric clusters in 1:2 and 2:1 ratio and tetrameric clusters in 2:2 ratio are also studied (Fig. 3). The HB

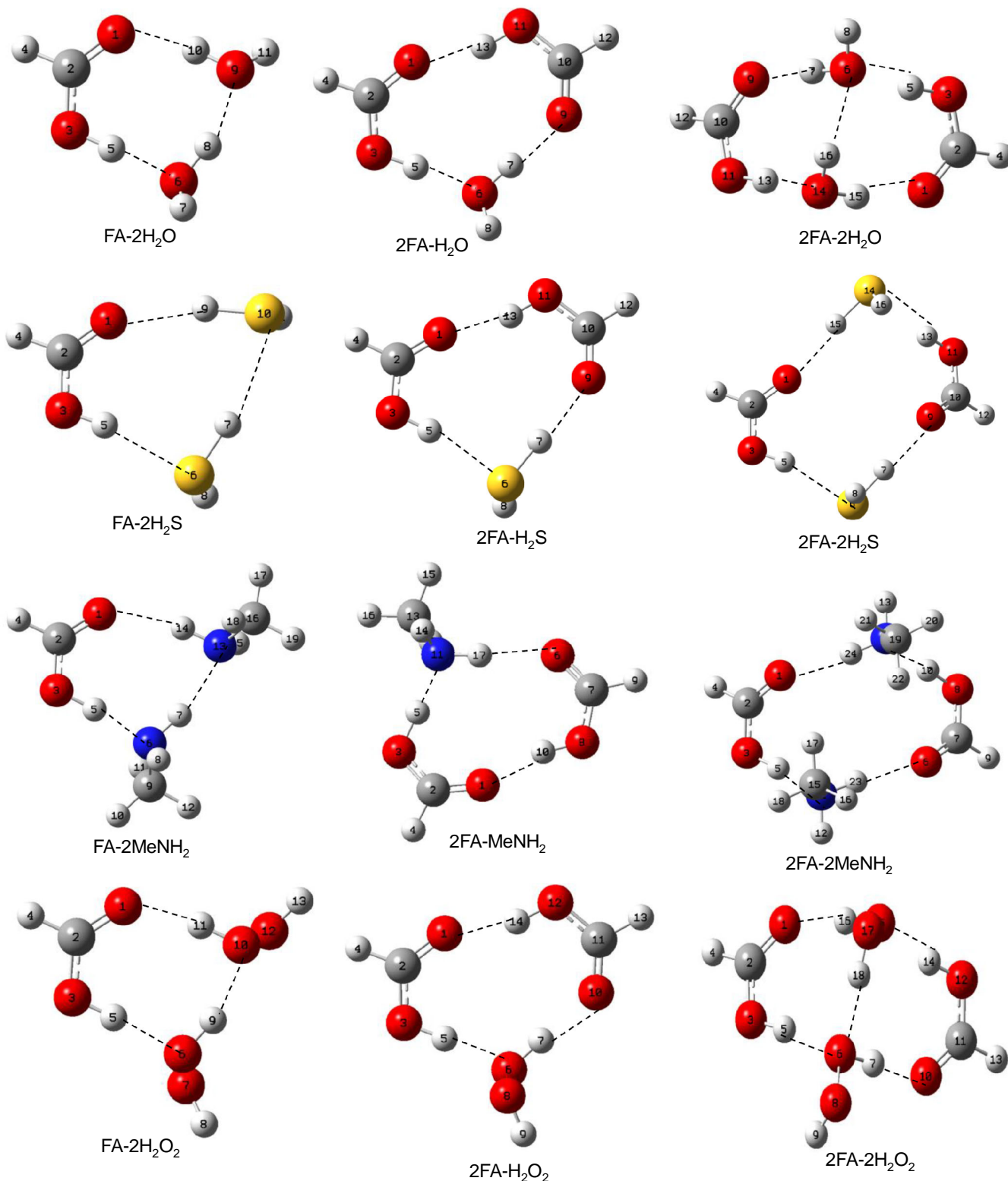


Fig. 3. Growth of clusters involving FA containing particles optimized at B3LYP/aug-cc-pVDZ level

parameters and binding energies of trimeric and tetrameric clusters are reported in Table-4. An important result that follows is that the system become more and more stable as large as the cluster is growing up. Increased number and strength of hydrogen bonds in tetramers than trimer which is in turn more than dimer increases overall stability of clusters. The most stable dimeric clusters (except MeNH<sub>2</sub>) involve formation of six membered ring structure on interaction of two subunits. Trimeric clusters of type 1:2 involve formation of 8-membered ring while 2:1 clusters involve formation of 10-membered and ring size increases to 12 members in case of tetrameric clusters (2:2) in all cases of selected nucleation precursors. The more is the number of atoms participating in formation of ring like structure, more stable is the cluster. The S.E. of tetrameric

complexes of formic acid with H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub> (with 5 O...H hydrogen bonds), is nearly similar and in these clusters, not only H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub> interact with formic acid but H<sub>2</sub>O-H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub>-H<sub>2</sub>O<sub>2</sub> interactions are observed in 2FA-2H<sub>2</sub>O and 2FA-2H<sub>2</sub>O<sub>2</sub> complex respectively. Hence, 12-membered bigger ring encloses two smaller 8 member rings due to HB interaction of H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub> among themselves in their respective clusters.

The dimer, trimer and tetramer cluster of formic acid with H<sub>2</sub>O/H<sub>2</sub>S/H<sub>2</sub>O<sub>2</sub> is less stable than MeNH<sub>2</sub> containing complexes. The clusters of formic acid with H<sub>2</sub>S have minimum stability and clusters of formic acid with MeNH<sub>2</sub> have largest stability. In case of 2FA-MeNH<sub>2</sub>, an eight membered ring is formed through two formic acid and MeNH<sub>2</sub> and made up of three HBs of length 1.519 Å, 1.693 Å and 1.946 Å successively. In

TABLE-4  
IMPORTANT HYDROGEN BONDING PARAMETERS, HYDROGEN BOND DISTANCES, HYDROGEN BOND ANGLES CALCULATED BINDING ENERGY (BE), ZERO-POINT VIBRATIONAL ENERGY (ZPE), FOR THE TRIMER AND TETRAMER COMPLEXES (298 K AND 1 atm) AT B3LYP/aug-cc-pVDZ (L1) AND AT THE MP2/aug-cc-pVDZ/B3LYP/aug-cc-pVDZ (L2) THEORETICAL LEVEL

Conformer	Hydrogen bonded distances (Å)		Hydrogen bonded angles (°)		B.E. (L1)	ZPVE (L1)	CP corr. B.E.	BSSE	B.E. (L2)
FA-2H <sub>2</sub> O	O6...H5	1.647	O6...H5-O3	177.4	-20.96	4.90	-22.26	0.94	-22.33
	O9...H8	1.739	O9...H8-O6	160.2					
	O1...H10	1.807	O1...H10-O9	165.9					
2FA-H <sub>2</sub> O	O6...H5	1.601	O6...H5-O3	176.0	-23.50	3.81	-26.00	1.14	-24.74
	O9...H7	1.735	O9...H7-O6	178.6					
	O1...H13	1.704	O1...H13-O11	163.4					
2FA-2H <sub>2</sub> O	O6...H5	1.699	O6...H5-O3	173.9	-32.71	6.56	-35.51	1.66	-35.59
	O9...H7	1.701	O9...H7-O6	176.2					
	O14...H13	1.591	O14...H13-O11	177.2					
	O1...H15	1.821	O1...H15-O14	168.3					
	O6...H16	2.120	O6...H16-O14	133.7					
FA-2H <sub>2</sub> S	O1...H9	2.185	O1...H9-S10	167.3	-7.98	2.76	-7.81	0.62	-11.46
	S10...H7	2.641	S10...H7-S6	165.1					
	S6...H5	2.351	S6...H5-O3	170.7					
2FA-H <sub>2</sub> S	S6...H5	2.252	S6...H5-O3	171.1	-14.38	2.79	-15.10	0.89	-17.51
	O9...H7	2.008	O9...H7-S6	178.1					
	O1...H13	1.784	O1...H13-O11	163.7					
2FA-2H <sub>2</sub> S	S6...H5	2.321	S6...H5-O3	167.8	-14.39	3.54	-14.36	0.98	-19.37
	O9...H7	2.096	O9...H7-S6	178.6					
	S14...H13	2.307	S14...H13-O11	171.9					
	O1...H15	2.107	O1...H15-S14	175.9					
	O1...H14	2.096	O1...H14-N13	161.9					
FA-2MeNH <sub>2</sub>	N6...H5	1.607	N6...H5-O3	175.3	-19.79	2.69	-22.44	1.09	-23.72
	N13...H7	2.044	N13...H7-N6	163.8					
	O1...H10	1.693	O1...H10-O8	164.6					
2FA-MeNH <sub>2</sub>	O6...H17	1.946	O6...H17-N11	176.7	-24.93	2.33	-31.49	1.29	-27.83
	O11...H5	1.519	O11...H5-O3	174.5					
	O1...H24	1.974	O1...H24-N14	173.3					
2FA-2MeNH <sub>2</sub>	N11...H5	1.562	N11...H5-O3	175.6	-33.92	3.44	-41.69	1.87	-40.60
	O6...H23	1.974	O6...H23-N11	173.3					
	N14...H10	1.562	N14...H10-O8	175.6					
	O1...H11	1.743	O1...H11-O10	166.6					
	O10...H9	1.760	O10...H9-O6	157.1					
FA-2H <sub>2</sub> O <sub>2</sub>	O6...H5	1.705	O6...H5-O3	177.8	-19.70	3.43	-20.49	1.21	-22.82
	O6...H5	1.651	O6...H5-O3	175.4					
	O10...H7	1.680	O10...H7-O6	177.4					
2FA-H <sub>2</sub> O <sub>2</sub>	O1...H14	1.700	O1...H14-O12	163.5	-22.94	3.22	-25.17	1.26	-25.38
	O10...H7	1.631	O10...H7-O6	177.6					
	O1...H16	1.754	O1...H16-O15	174.6					
2FA-2H <sub>2</sub> O <sub>2</sub>	O15...H14	1.642	O15...H14-O12	171.9	-30.70	5.09	-34.16	2.08	-35.91
	O6...H5	1.747	O6...H5-O3	173.6					
	O6...H18	1.956	O6...H18-O17	151.0					
	O10...H7	1.631	O10...H7-O6	177.6					
	O1...H16	1.754	O1...H16-O15	174.6					



this cluster, the strength of HB between formic acid and MeNH<sub>2</sub> seems to be more than dimeric cluster as well as FA-2MeNH<sub>2</sub> cluster. The molecular interactions in 2FA-MeNH<sub>2</sub> can be divided into three constituent types (i) Acid-Acid: O...H-O in which one formic acid is HB acceptor, other formic acid is HB donor; (ii) Acid-base: O...H-N in which formic acid is HB acceptor, MeNH<sub>2</sub> is HB donor; (iii) Base-Acid: N...H-O in which MeNH<sub>2</sub> is HB acceptor and formic acid is HB donor. Similarly in clusters of type FA-2MeNH<sub>2</sub>, the three type of molecular interactions are (i) Acid-base O...H-N; (ii) Base-Base N...H-N; and (iii) Base-Acid N...H-O interaction. Another conclusion derived is that since largest S.E. arises on interaction of formic acid with MeNH<sub>2</sub>. Thus more is the number of acid-base interactions, more stable it is when particle is growing up.

As mentioned earlier, the B.E. calculated for dimeric cluster namely (MeNH<sub>2</sub>)<sub>2</sub>, (H<sub>2</sub>O)<sub>2</sub>, (H<sub>2</sub>S)<sub>2</sub>, (H<sub>2</sub>O<sub>2</sub>)<sub>2</sub> show that B.E. is less than (FA)<sub>2</sub>. Thus for trimeric clusters of formic acid with selected molecules in two different ratio *i.e.* 1:2 and 2:1, it can be concluded that more the number of formic acid in cluster, larger is the stability of species. Hence, 2FA-MeNH<sub>2</sub>/H<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>S are more stable than FA-2MeNH<sub>2</sub>/H<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>S. The B.E. in 2FA·MeNH<sub>2</sub> *versus* FA·2MeNH<sub>2</sub> is -27.8 *vs.* -23.7, in case of 2FA·H<sub>2</sub>O *vs.* FA·2H<sub>2</sub>O is -24.7 *vs.* -22.3. Similar values for clusters of formic acid with H<sub>2</sub>O<sub>2</sub> are -25.4 and -22.8 and with H<sub>2</sub>S is -17.5 *vs.* -11.5 kcal/mol. The general decreasing order of stability of (FA: nucleating precursors) clusters is 2:2 > 2:1 > 1:2 > 1:1

**Frequency analysis:** Table-2 displays change in length of bonds involved in hydrogen bonding ( $\Delta d$  in Å) and change in stretching frequencies ( $\Delta \nu$  in cm<sup>-1</sup>) of HB donor upon complexation relative to monomers and the IR intensities of vibrations. The complex formation of formic acid with H<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>S and MeNH<sub>2</sub> leads to production of new degrees of freedom and thus new vibrational modes are seen, which not earlier present in monomeric species were. The trimeric and tetrameric clusters have even more vibrational modes due to three body and four body molecular interactions resulting in stable complexes. The calculated data shows that the frequencies and IR intensities of bonds involved in hydrogen bonding are most significantly affected on complexation. A large frequency red shift is mainly observed for vibration of bonds involved in HB formation. Upon complex formation, O-H of formic acid as HB donor in conventional O-H...O, O-H...S, O-H...N is red shifted due to which  $\nu(\text{O-H})$  decrease and there is lengthening of O-H bond which is in sharp contrast to non-conventional C-H...O and C-H...N in FA-H<sub>2</sub>O-C and FA-MeNH<sub>2</sub>-B. The C-H as HB donor is usually blue shifted hence frequency of C-H bond increases by 28.17 and 18.05 cm<sup>-1</sup> and there is shortening of C-H bond by 0.002 Å in both cases. In the IR of FA-H<sub>2</sub>O-A, red shift of 401.2 cm<sup>-1</sup> is observed for OH stretching of formic acid subunit. The O-H stretching vibration is decreased to 3316 cm<sup>-1</sup> in complex relative to 3717.2 cm<sup>-1</sup> in isolated formic acid. For the selected molecules, minimum red shift of 242 cm<sup>-1</sup> is observed in FA-H<sub>2</sub>S-A for O-H bond of formic acid upon interaction with H<sub>2</sub>S. The O-H and S-H stretching frequency of H<sub>2</sub>O and H<sub>2</sub>S is decreased by only 173.3 and 24.96 cm<sup>-1</sup>,

respectively in the dimeric clusters FA-H<sub>2</sub>O-A and FA-H<sub>2</sub>S-A pointing to less strong participation of H<sub>2</sub>O and H<sub>2</sub>S in bonding as compared to formic acid. The FA-MeNH<sub>2</sub>-A complex has larger number of vibrational modes due to more number of atoms and bonds in the complex formation. In this cluster when the O-H group from formic acid subunit in the complex is compared to the isolated formic acid, it is seen that frequency is red shifted by 930.69 cm<sup>-1</sup> and is accompanied by huge increase in IR absorption.

The order of  $\Delta \nu$  in most stable dimer complexes follows the order MeNH<sub>2</sub> > H<sub>2</sub>O<sub>2</sub> > H<sub>2</sub>O > H<sub>2</sub>S, the  $\Delta \nu$  being -930.69, -431.62, -401.21, -242.23 cm<sup>-1</sup>. The order of  $\Delta \nu$  correlates well with corresponding change in O-H bond length (0.047 Å, 0.021 Å, 0.020 Å, 0.011 Å) respectively in these clusters. As stated earlier, the order of stability of formic acid dimeric clusters with selected molecules under study is MeNH<sub>2</sub> > H<sub>2</sub>O<sub>2</sub> > H<sub>2</sub>O > H<sub>2</sub>S. The S.E. of clusters also corroborates with frequency shift ( $\Delta \nu$ ). When cluster grow to trimer and tetramers, the B.E. of H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub> with formic acid is comparable. In trimeric complexes, FA-2H<sub>2</sub>O, FA-2H<sub>2</sub>O<sub>2</sub>, FA-2H<sub>2</sub>S, FA-2MeNH<sub>2</sub>, the  $\Delta \nu$  of O-H of FA is -688.0, -563.6, -307.6, -1334.7 cm<sup>-1</sup> respectively, which again suggests strong binding of MeNH<sub>2</sub> than other nucleating precursors.

**NBO analysis:** NBO analysis has been employed to compute 2<sup>nd</sup> order perturbation energies E<sup>(2)</sup> values associated with electron delocalization between HB donor and HB acceptor. Analysis of E<sup>(2)</sup> of dimeric complexes of formic acid with H<sub>2</sub>O, H<sub>2</sub>S, H<sub>2</sub>O<sub>2</sub>, MeNH<sub>2</sub> (Table-5) shows that for most stable dimeric complexes the order of E<sup>(2)</sup> for H<sub>2</sub>O, MeNH<sub>2</sub>, H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>S as HB acceptors for nX X=(O,N,S)→σ\* O3-H5 (FA) decreases in order MeNH<sub>2</sub> > H<sub>2</sub>O<sub>2</sub> > H<sub>2</sub>O > H<sub>2</sub>S with E<sup>(2)</sup> values being 37.45, 22.69, 19.99, 11.67 kcal/mol, respectively. This order is also in agreement with observed trend of B.E. order of dimeric complexes. The larger is the E<sup>(2)</sup> value, the stronger is the interaction between HB donor and acceptor orbitals and hence larger S.E. arises from electron delocalization. With increased number of donor acceptor units, tetrameric clusters have larger E<sup>(2)</sup> values than trimeric clusters which in turn have larger E<sup>(2)</sup> than dimeric cluster. In FA-H<sub>2</sub>O<sub>2</sub>-A, the O-H of H<sub>2</sub>O<sub>2</sub> exhibit -I effect, which is responsible for strong nO (FA)→σ\* O-H (H<sub>2</sub>O<sub>2</sub>) with E<sup>(2)</sup> of 18.68 kcal/mol. For FA-H<sub>2</sub>O-A and FA-H<sub>2</sub>S-A complex E<sup>(2)</sup> value of similar delocalization is 5.56 and 1.01 kcal/mol respectively. The NBO delocalizations for studied clusters suggest MeNH<sub>2</sub> is strongest HB acceptor, H<sub>2</sub>O<sub>2</sub> is both HB acceptor and donor while H<sub>2</sub>S is weak HB donor and acceptor.

It is widely accepted that for red shifted X-H...Y electron density is transferred from lone pair (LP) of HB acceptor Y to antibonding σ\* of HB donor X-H upon HB cluster formation which leads to weakening and elongation of X-H bond. In present study, considerable electron density shift occurs from LP of H<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>S, MeNH<sub>2</sub> as evident from largest E<sup>(2)</sup> value of 59.45 kcal/mol in tetrameric FA-MeNH<sub>2</sub> interaction. For most stable clusters of formic acid with MeNH<sub>2</sub>, charge transfer (CT) leads to weakening and elongation of O-H bond of formic acid, which is in accordance with significantly larger frequency shifts observed in O-H stretching frequency (from

TABLE-5  
SECOND ORDER DELOCALIZATION ENERGIES ( $E^{(2)}$ , kcal/mol) ASSOCIATED WITH  
ORBITAL INTERACTIONS FOR VARIOUS HYDROGEN BONDED COMPLEXES AT L1 LEVEL

Complexes	Orbital interaction	$E^{(2)}$	Complexes	Orbital interaction	$E^{(2)}$	Complexes	Orbital interaction	$E^{(2)}$
FA-H <sub>2</sub> O-A	$n_{O1} \rightarrow \sigma^*_{H6-O7}$	5.56	FA-2H <sub>2</sub> O	$n_{O6} \rightarrow \sigma^*_{O3-H5}$	33.42	FA-2MeNH <sub>2</sub>	$n_{O1} \rightarrow \sigma^*_{N13-H14}$	6.22
	$n_{O7} \rightarrow \sigma^*_{O3-H5}$	19.99		$n_{O9} \rightarrow \sigma^*_{O6-H8}$	21.04		$n_{N6} \rightarrow \sigma^*_{O3-H5}$	51.13
FA-H <sub>2</sub> O-B	$n_{O1} \rightarrow \sigma^*_{H6-O7}$	5.25		$n_{O1} \rightarrow \sigma^*_{O9-H10}$	15.38		$n_{N13} \rightarrow \sigma^*_{N6-H7}$	12.58
FA-H <sub>2</sub> O-C	$n_{O3} \rightarrow \sigma^*_{H6-O7}$	1.31	2FA-H <sub>2</sub> O	$n_{O6} \rightarrow \sigma^*_{O3-H5}$	37.94	2FA-MeNH <sub>2</sub>	$n_{O1} \rightarrow \sigma^*_{O8-H10}$	24.66
FA-H <sub>2</sub> S-A	$n_{O1} \rightarrow \sigma^*_{S6-H7}$	1.01		$n_{O9} \rightarrow \sigma^*_{O6-H7}$	20.61		$n_{O6} \rightarrow \sigma^*_{N11-H17}$	11.77
	$n_{S6} \rightarrow \sigma^*_{O3-H5}$	11.67		$n_{O1} \rightarrow \sigma^*_{O11-H13}$	23.89		$n_{N11} \rightarrow \sigma^*_{O3-H5}$	68.40
FA-H <sub>2</sub> S-B	$n_{O1} \rightarrow \sigma^*_{H6-S7}$	4.73	2FA-2H <sub>2</sub> O	$n_{O6} \rightarrow \sigma^*_{O3-H5}$	27.54	2FA-2MeNH <sub>2</sub>	$n_{O1} \rightarrow \sigma^*_{N14-H24}$	7.20
FA-H <sub>2</sub> S-C	$n_{O3} \rightarrow \sigma^*_{H6-O7}$	0.88		$n_{O9} \rightarrow \sigma^*_{O6-H7}$	25.19		$n_{N11} \rightarrow \sigma^*_{O3-H5}$	59.44
FA-H <sub>2</sub> O <sub>2</sub> -A	$n_{O1} \rightarrow \sigma^*_{O7-H8}$	18.68		$n_{O14} \rightarrow \sigma^*_{O11-H13}$	41.59		$n_{O6} \rightarrow \sigma^*_{N11-H23}$	7.20
	$n_{O6} \rightarrow \sigma^*_{O3-H5}$	22.69		$n_{O1} \rightarrow \sigma^*_{O14-H15}$	14.8		$n_{N14} \rightarrow \sigma^*_{O8-H10}$	59.45
FA-H <sub>2</sub> O <sub>2</sub> -B	$n_{O6} \rightarrow \sigma^*_{O3-H5}$	13.85	FA-2H <sub>2</sub> S	$n_{O6} \rightarrow \sigma^*_{O14-H16}$	3.94	FA-2H <sub>2</sub> O <sub>2</sub>	$n_{O1} \rightarrow \sigma^*_{O10-H11}$	22.31
	$n_{O1} \rightarrow \sigma^*_{O6-H9}$	8.55		$n_{O1} \rightarrow \sigma^*_{H9-S10}$	4.56		$n_{O10} \rightarrow \sigma^*_{O6-H9}$	20.65
FA-H <sub>2</sub> O <sub>2</sub> -C	$n_{O1} \rightarrow \sigma^*_{H6-O7}$	12.34		$n_{S10} \rightarrow \sigma^*_{S6-H7}$	6.28		$n_{N6} \rightarrow \sigma^*_{O3-H5}$	26.16
FA-H <sub>2</sub> O <sub>2</sub> -D	$n_{O3} \rightarrow \sigma^*_{H6-O7}$	5.38		$n_{S6} \rightarrow \sigma^*_{O3-H5}$	14.95	2FA-H <sub>2</sub> O <sub>2</sub>	$n_{N6} \rightarrow \sigma^*_{O3-H5}$	31.11
FA-MeNH <sub>2</sub> -A	$n_{N6} \rightarrow \sigma^*_{O3-H5}$	37.45	2FA-H <sub>2</sub> S	$n_{S6} \rightarrow \sigma^*_{O3-H5}$	20.96		$n_{O10} \rightarrow \sigma^*_{O6-H7}$	28.56
FA-MeNH <sub>2</sub> -C	$n_{O1} \rightarrow \sigma^*_{H6-N7}$	1.36		$n_{O9} \rightarrow \sigma^*_{S6-H7}$	9.93		$n_{O1} \rightarrow \sigma^*_{O12-H14}$	24.43
	$n_{N7} \rightarrow \sigma^*_{C2-H4}$	1.72		$n_{O1} \rightarrow \sigma^*_{O11-H13}$	15.48	2FA-2H <sub>2</sub> O <sub>2</sub>	$n_{O10} \rightarrow \sigma^*_{O6-H7}$	36.08
(H <sub>2</sub> O) <sub>2</sub>	$n_{O4} \rightarrow \sigma^*_{O1-H3}$	9.66	2FA-2H <sub>2</sub> S	$n_{S6} \rightarrow \sigma^*_{O3-H5}$	16.55		$n_{O1} \rightarrow \sigma^*_{O15-H16}$	20.98
(H <sub>2</sub> O) <sub>2</sub>	$n_{O2} \rightarrow \sigma^*_{O7-H8}$	11.53		$n_{O9} \rightarrow \sigma^*_{S6-H7}$	4.66		$n_{O15} \rightarrow \sigma^*_{O12-H14}$	29.95
	$n_{O5} \rightarrow \sigma^*_{O1-H4}$	11.54		$n_{S14} \rightarrow \sigma^*_{O11-H13}$	17.35		$n_{O6} \rightarrow \sigma^*_{O3-H5}$	20.35
(H <sub>2</sub> S) <sub>2</sub>	$n_{S4} \rightarrow \sigma^*_{S1-H3}$	3.10		$n_{O1} \rightarrow \sigma^*_{S14-H15}$	4.89		$n_{O6} \rightarrow \sigma^*_{O17-H18}$	8.97
(MeNH <sub>2</sub> ) <sub>2</sub>	$n_{N9} \rightarrow \sigma^*_{N1-H4}$	5.72						

3717.2 to 2786.6 cm<sup>-1</sup>) in dimeric 1:1, 3717.2 to 2382.6 cm<sup>-1</sup> in trimeric (1:2) and 3717.2 to 2003.4 cm<sup>-1</sup> in one unit and 3717.2 to 3282.4 cm<sup>-1</sup> in 2<sup>nd</sup> unit in trimeric (2:1) and red shift of 1507.8 to 1536.3 cm<sup>-1</sup> in 2:2 tetrameric complexes.

Larger  $E^{(2)}$  value of FA as HB donor towards O, S, N of water, peroxide, sulphide, methylamine serving as HB acceptor and relatively lower  $E^{(2)}$  value for reverse charge transfer delocalization lead to conclusion that electron gaining tendency of FA is significantly more than water, H<sub>2</sub>S, MeNH<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>. As expected, The  $E^{(2)}$  value are lower for orbital delocalization for unconventional HBs of type  $nN \rightarrow \sigma^* C-H$  in FA-MeNH<sub>2</sub>-A and  $nS \rightarrow \sigma^* S-H$  in FA-2H<sub>2</sub>S, which are generally weak in nature.

In dimeric complexes FA-H<sub>2</sub>O-B, FA-H<sub>2</sub>S-B, FA-H<sub>2</sub>S-C, FA-H<sub>2</sub>O<sub>2</sub>-C, FA-H<sub>2</sub>O<sub>2</sub>-D, FA-MeNH<sub>2</sub>-A there is only one delocalization. FA acts as HB acceptor in first five mentioned dimeric clusters while MeNH<sub>2</sub> acts as HB acceptor in FA-MeNH<sub>2</sub>-A. The  $nO(FA) \rightarrow \sigma^* O-H$  (H<sub>2</sub>O/H<sub>2</sub>O<sub>2</sub>) orbital interaction in FA-H<sub>2</sub>O-A has  $E^{(2)}$  value lower in comparison to similar orbital interaction in FA-H<sub>2</sub>O<sub>2</sub>-A.

**Charges:** Electrostatic interactions associated with HB complexes have been studied through natural population analysis (NPA) charges obtained from NBO analysis. The electrostatic interactions are favoured by high positive and negative charges on atoms involved in hydrogen bonding. Atomic charges on HB donor and HB acceptor atom calculated at L1 level are tabulated in Table-6. The O atom of H<sub>2</sub>O and N of MeNH<sub>2</sub> has high negative charge as compared to O of H<sub>2</sub>O<sub>2</sub> and in addition S of H<sub>2</sub>S has very less negative charge. It can be said that electrostatic component of hydrogen bonding is

larger in complexes of formic acid with H<sub>2</sub>O and MeNH<sub>2</sub> while bonds to H<sub>2</sub>S are mainly governed by charge transfer. The increase in positive charge on hydrogen atom and negative charge on HB acceptor atom is observed upon HB formation. High charge on atoms involved in hydrogen bonding, larger  $E^{(2)}$  values and short HB distance all indicate larger contribution of  $X6 \cdots H5-O3$  (X is HB acceptor of H<sub>2</sub>O, H<sub>2</sub>S, H<sub>2</sub>O<sub>2</sub>, MeNH<sub>2</sub>) towards stabilization.

## Conclusion

Quantum chemical methods have been employed to investigate formic acid as a source of new particle formation (NPF) by studying the structural features, nature of interactions between each component, interaction energies of the hydrogen bonded clusters (dimers, trimers and tetramers) of formic acid with atmospheric nucleation precursors like H<sub>2</sub>O, H<sub>2</sub>S, MeNH<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> at ambient and tropospheric conditions. Cluster formation is accompanied by increased charge transfer, increased charges on donor/Acceptor atoms, red shifts and increased IR intensity in clusters. The Gibbs free energy of formation of FA-FA, FA-H<sub>2</sub>S and FA-H<sub>2</sub>O<sub>2</sub>, FA-H<sub>2</sub>O dimer complexes are all positive in this study. Positive free energies indicating that the clusters studied are not thermodynamically stable at 298 K. Free energy barrier is needed to be crossed before vapour to liquid/solid become spontaneous. But at tropospheric (low temperature) conditions, the dimer, trimer and tetramer clusters of formic acid with H<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub>, MeNH<sub>2</sub> all have negative binding free energy and hence are thermodynamically stable and formed spontaneously and favourably. The enthalpy of formation of clusters was found to decrease with increase in atmospheric

TABLE-6  
ATOMIC CHARGES OBTAINED FROM NATURAL BOND ORBITAL (NBO)  
ANALYSIS FOR HYDROGEN BONDED CLUSTERS AT L1 LEVEL

Species	Atomic charges	Species	Atomic charges
(H <sub>2</sub> O) <sub>2</sub>	O4(H3) -0.967(0.497)	FA-2H <sub>2</sub> S	O1(H9) -0.650(0.195)
(H <sub>2</sub> S) <sub>2</sub>	S4(H3) -0.309(0.163)		S10(H7) -0.332(0.177)
(MeNH <sub>2</sub> ) <sub>2</sub>	N9(H4) -0.916(0.395)		S6(H5) -0.321(0.499)
(H <sub>2</sub> O <sub>2</sub> ) <sub>2</sub>	O5(H4) -0.496(0.488)	2FA-H <sub>2</sub> S	S6(H5) -0.331(0.497)
	O2(H8) -0.496(0.488)		O9(H7) -0.660(0.210)
(FA) <sub>2</sub>	O1(H6) -0.680(0.528)		O1(H13) -0.686(0.536)
	O10(H5) -0.680(0.528)	2FA-2H <sub>2</sub> S	S6(H5) -0.331(0.501)
FA-H <sub>2</sub> O-A	O1(H6) -0.661(0.517)		O9(H7) -0.658(0.207)
	O7(H5) -0.988(0.528)		S14(H13) -0.328(0.500)
FA-H <sub>2</sub> O-B	O1(H6) -0.639(0.497)		O1(H15) -0.658(0.207)
FA-H <sub>2</sub> O-C	O3(H6) -0.746(0.492)	FA-2MeNH <sub>2</sub>	H14(O1) 0.418(-0.685)
	O7(H4) -0.977(0.158)		H5(N6) 0.507(-0.931)
FA-H <sub>2</sub> S-A	O1(H7) -0.635(0.189)		H7(N13) 0.430(-0.944)
	S6(H5) -0.318(0.499)	2FA-MeNH <sub>2</sub>	H10(O1) 0.539(-0.721)
FA-H <sub>2</sub> S-B	O1(H6) -0.622(0.176)		H17(O6) 0.439(-0.678)
FA-H <sub>2</sub> S-C	O3(H6) -0.735(0.165)		H5(O11) 0.503(-0.916)
FA-H <sub>2</sub> O <sub>2</sub> -A	O1(H8) -0.663(0.499)	2FA-2MeNH <sub>2</sub>	H24(O1) 0.440(-0.708)
	O6(H5) -0.506(0.519)		H5(N11) 0.505(-0.917)
FA-H <sub>2</sub> O <sub>2</sub> -B	O1(H9) -0.650(0.512)		H23(O6) 0.440(-0.708)
	O6(H5) -0.519(0.516)		H10(N14) 0.505(-0.917)
FA-H <sub>2</sub> O <sub>2</sub> -C	O1(H6) -0.648(0.493)	FA-2H <sub>2</sub> O <sub>2</sub>	H11(O1) 0.518(-0.682)
FA-H <sub>2</sub> O <sub>2</sub> -D	O3(H6) -0.757(0.485)		H9(O10) 0.514(-0.523)
FA-MeNH <sub>2</sub> -A	N6(H5) -0.918(0.512)		H5(O6) 0.519(-0.522)
FA-MeNH <sub>2</sub> -B	O1(H6) -0.633(0.388)	2FA-H <sub>2</sub> O <sub>2</sub>	H5(O6) 0.522(-0.524)
	N7(H4) -0.927(0.159)		H7(O10) 0.522(-0.681)
FA-2H <sub>2</sub> O	O6(H5) -0.996(0.529)		H14(O1) 0.538(-0.701)
	O9(H8) -1.003(0.526)	2FA-2H <sub>2</sub> O <sub>2</sub>	H7(O10) 0.526(-0.690)
	O1(H10) -0.686(0.523)		H16(O1) 0.525(-0.669)
2FA-H <sub>2</sub> O	O6(H5) -0.996(0.532)		H14(O15) 0.526(-0.537)
	O9(H7) -0.686(0.530)		H5(O6) 0.519(-0.555)
	O1(H13) -0.702(0.538)		H18(O6) 0.484(-0.555)
2FA-2H <sub>2</sub> O	O6(H5) -1.023(0.529)	FA	O1 (H5) -0.610 (0.504)
	O9(H7) -0.702(0.533)	H <sub>2</sub> O	O1 -0.957
	O14(H13) -0.989(0.528)		H2 0.478
	O1(H15) -0.675(0.527)		H3 0.478
	O6(H16) -1.023(0.510)	MeNH <sub>2</sub>	N1 -0.910
		H <sub>2</sub> S	S1 -0.312
			H2 0.156
			H3 0.156

altitude. Results indicated that growth of clusters from dimer to trimer to tetramer increased overall stability of complex through increased number and strength of hydrogen bonds. The tetramer complexes (2:2) are more stable than trimer (1:2 and 2:1), which in turn is more stable than dimeric 1:1 complexes in all the clusters of formic acid with selected nucleating species. E<sup>(2)</sup> values from NBO analysis indicate that electron gaining tendency of formic acid is remarkably more than H<sub>2</sub>O, H<sub>2</sub>S, MeNH<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>. The usage of large basis set reduces BSSE in the clusters. Maximum stabilizing effect is observed in case of MeNH<sub>2</sub> where clusters are spontaneously formed at ambient as well as tropospheric conditions. Theoretical calculations show that O-H...N interactions contribute more to stability of complexes. The relatively less electronegative N with enhanced basicity due to presence of methyl group results in largest S.E, whereas clusters of H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub> have comparable S.E. and minimum S.E. is observed for clusters of formic acid with H<sub>2</sub>S. The decreasing order of stability of clusters of

formic acid with H<sub>2</sub>O, H<sub>2</sub>S, H<sub>2</sub>O<sub>2</sub>, MeNH<sub>2</sub> was 2:2 > 2:1 > 1:2 > 1:1. More is the number of formic acid in the cluster, larger is the stability.

#### CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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