ICRTST-2018 S.S.S.K.R. Innani Mahavidyalaya Karanja (Lad)
Relevant Conference Themes:
Mathematical Physical & Chemical Sciences, Computer Science, Information Technology

Theory, Computation and Simulations can be Stand Alone Methodology as much as the Reproducible Experimental Determination of Physical Quantities.

By
Sankarampadi Aravamudhan
Department of Chemistry
NORTH EASTERN HILL UNIVERSITY
SHILLONG 793022 MEGHALAYA
INDIA
saravamudhan@hotmail.com

Keywords: Quantum Theory, Quantum Mechanical Methods, Computational Chemistry, Calculation of Physical Quantities, Theoretical Modelling of Physical Systems, Simulation, Inferences on Trends, Insights into Phenomena and Mechanisms, Spectroscopic Techniques, Determination of Spectral Properties.

(**ABSTRACT** Text in -*492 words*- the following sheet)

ABSTRACT EXTENDED

Paper organization

ABSTRACT

Generally, with references to Chemical Sciences, theory is meant for explaining experimental observations, theoretical calculations are made to sort out experimentally observed anomalous trends and exceptional material characteristics besides in connection with the supportive spectroscopic features. Theory more are less gets validated by the extent to which the calculations and conclusions are helpful in interpreting experimental findings. The perspective in this contribution is to learn how to be consistent within the theoretical frame work and confidently establish trends in calculated results to gain insights into the physical systems under study so that these inferences can be transferred to the experimental domains to design novel experiments.
http://www.ugc-inno-nehu.com/ser-sa/SER-1-Stacking_benzene_dimer.doc
http://ugc-inno-nehu.com/ser-sa/SER-2-BD-HR-BENZ.doc
Three different instances are being enumerated to highlight the points of view as implied in the title of this contributed paper.

(1) The instance of reconciling with the fact that the PMR spectrum of a Polymer chain can become interpretable by invoking a cyclic dimeric structure referred to as the "fictitious spin book keeping" structure.
http://www.ugc-inno-nehu.com/events-2018.html#bhc

(2) The Quantum Mechanical Calculation for Geometry Optimization (G.O.) can handle not only isolated molecules, but also ensemble of structures. I certain cases when the G.O. is applied to an ensemble of molecules, this can conveniently indicate what is the energy optimized equilibrium arrangement of the ensemble of molecules, sometimes even unusual bonding between units or break up of units are possible when there are more number of identical units. Simple example to quote is a cluster of 'n' number of water molecules drawn in structure with arbitrary locations. In such a cluster of material mostly known in liquid state, random diffusions of various degrees of freedom are possible which have to be explicitly taken into account during the energy minimization applying calculus of variations. Such a requirement may be to get results by the G.O. calculations which are apparently much closer to reality.
http://www.ugc-inno-nehu.com/events-2017.html#E09

(3) To this context, two molecules of totally different compounds (which in reality are never considered together for forming useful compounds) can be drawn on structure editor and submitted for a Q.M. calculation of physical properties of the combined system. Certain quantities like the atomic charges, dipole moment and spectroscopic properties (specifically Proton NMR patterns) can reveal the possible nature of interactions which may be revealing certain trends for compounds which really matter in the laboratories.
http://www.ugc-inno-nehu.com/ISC105-OSU/isc105-doc.pdf

ABSTRACT EXTENDED

1. AN ELEMENTARY TOPICAL EXPOSURE WITH BENZENE DIMER

A beginning can be made with the simple case of benzene-dimer. The benzene dimer seems to be encountered in vapour state, and certain rotational constants, seems to have been amenable for experimental measurement by microwave pulsed-nozzle FT experiments. However, it is not at all difficult to draw two identical benzene molecules in varying relative disposition and calculate theoretically molecular properties. Three such dispositions are described and depicted below:

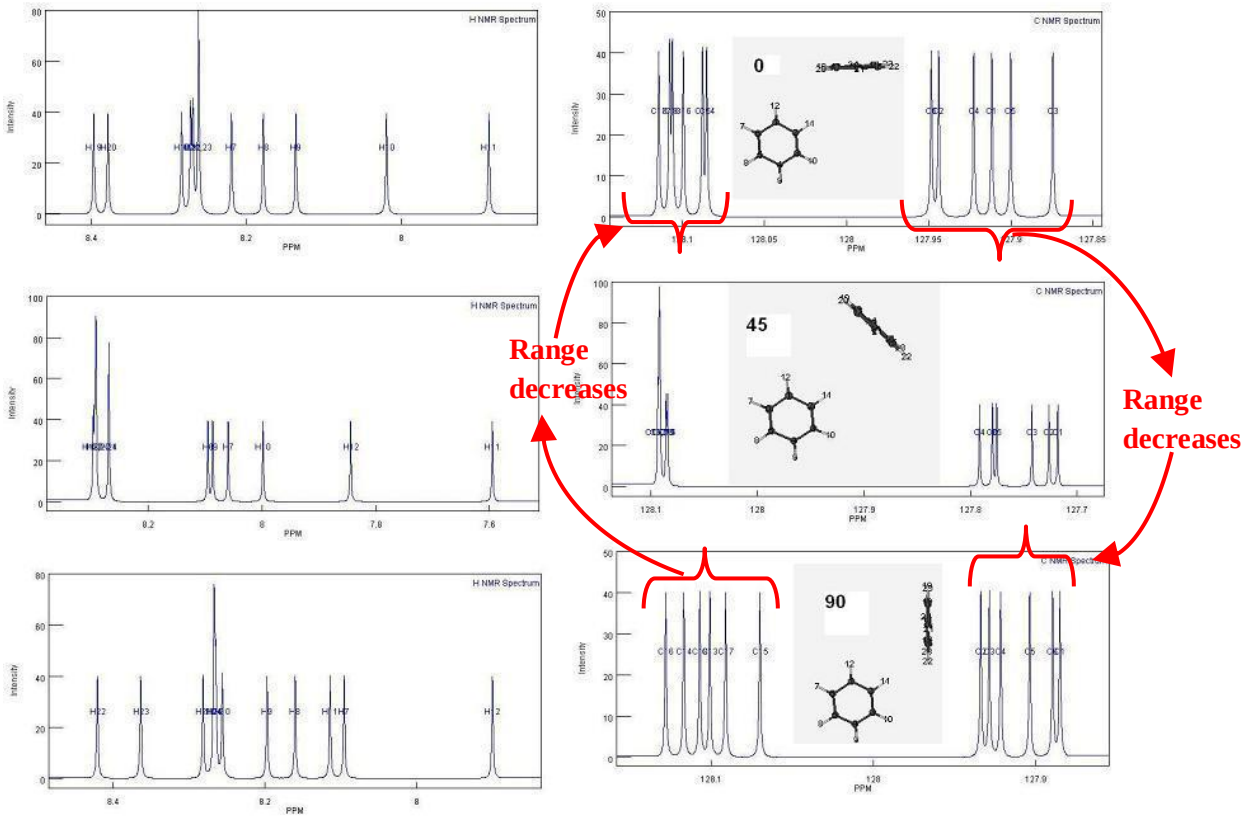

FIG.1 ***On the Left Hand Side, ^{1}H (proton) NMR is shown, and on the Right Hand Side, the ^{13}C calculated spectrum***.

The benzene dimers above were generated by first drawing an optimized benzene structure and then, copying the same, and pasting and placing at the appropriate centroid-separation distance. The inclination of one of the structure is changed with respect to a vertical axis; and thus the three different dispositions above were obtained. Each one of them submitted for NMR calculation without optimizing the dimer.

In the ^{13}C NMR, the two benzene molecules have grouped into two different ranges of Chemical shift. For ^{1}H NMR the pattern is so evident; Obvious changes in the range of chemical shifts of the rings are evidenced for the two rings in case of both nuclei.

Because the dimers are themselves not optimized, the term “motives” may not be applicable. Never the less the results are informative.

The importance of such calculations would be much more evident when non bonded aromatic rings occur in the neighbourhood of each other due to the secondary and tertiary structures of biological macro molecules. Typical contexts are described **(1)** in connection with occurrence of packing of aromatic rings against tryptophan residues in proteins. Generating patterns of such Calculated NMR spectra and cataloguing might be helpful in identifying relative orientations by using

crystallographic data, generating such structures in the structure editors and submitting them for NMR calculations. It may not be necessary to handle any such dimer structures experimentally and obtain NMR spectra from spectrometers.
THE NMR SPECTRA for this structure of DIMER can be simulated (2) using FTNMR Simulation software using the Chemical Shift values obtained from QM Calculations and the tabulated J coupling values for benzene protons at VARIOUS Magnetic Field values corresponding to proton frequency from 100MHz to 2000MHz (2 GHz). Commercial spectrometers currently available have a maximum frequency value 1GHz. Thus the value of simulated spectra is that most of the advantages of obtaining spectra at Higher fields would be available in frequency ranges in which

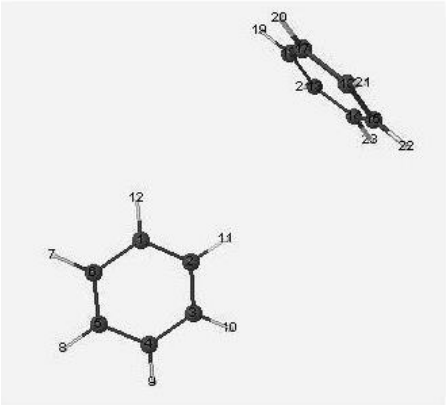

FIG.2 ***A dimeric structure for NMR Simulation (See Fig.3)***

one cannot obtain experimental spectra for want of spectrometers at such high fields. More over the calculated values of chemical shifts and the J values from tabulations can be used to simulate at higher fields to obtain simplified patterns for recognition of occurrences of aromatic ring stackings / packings. Such set of simulated spectra are depicted in **FIG.3**. The NMR Simulation software used for the calculations of spectra in **FIG.3** is from the link given in the webpage for nehu-saif **(3).** This illustrates the perspective QM Calculation together with spectral simulation can stand alone without the necessity to refer to experimental values.

2. A BIT MORE LEAD INTO THE TOPIC OF THE PAPER: POLYMER PMR

Having got an exposure to the theme of this contribution, a bit more lead into the implications of the theme would be possible by considering the case of styrene polymer, where a stand- alone theoretical result can substantiate the practically fictitious conjecture. To explain this case of polymeric styrene further, the PMR spectrum of a polymeric styrene could be explained and simulated convincingly by NMR spectral parameters attributable to a cyclic dimer of styrene. Thus this cyclic dimer structure which seemingly is a much simpler chemical structure as compared to the structure of the polymer is termed as “fictitious spin book keeping structure”. This further sounds as a strange situation when the literature search does not have any record of this particular dimeric isomer as a known compound but another isomer is well known.

Thus an effort could be made by optimizing a styrene isolated molecule to obtain a convincingly stable equilibrium structure and draw two such identical molecules conveniently poised or forming a dimer when the two molecules are subjected to Geometry optimization. If the dimer is more stable than two identical monomers, the variation principle should lead **(FIG.4.)** to the more stable

configuration for the two molecules together. In such a case what is the resulting isomeric conformations and for that resulting stable dimer what are the chemical shift values obtained by QM calculation and how the simulated spectrum would look in comparison to the experimental spectrum **(FIG.5.)**. This also would indicate a reason if anything specific exists, as to why this compound is not known in literature. **(4)**

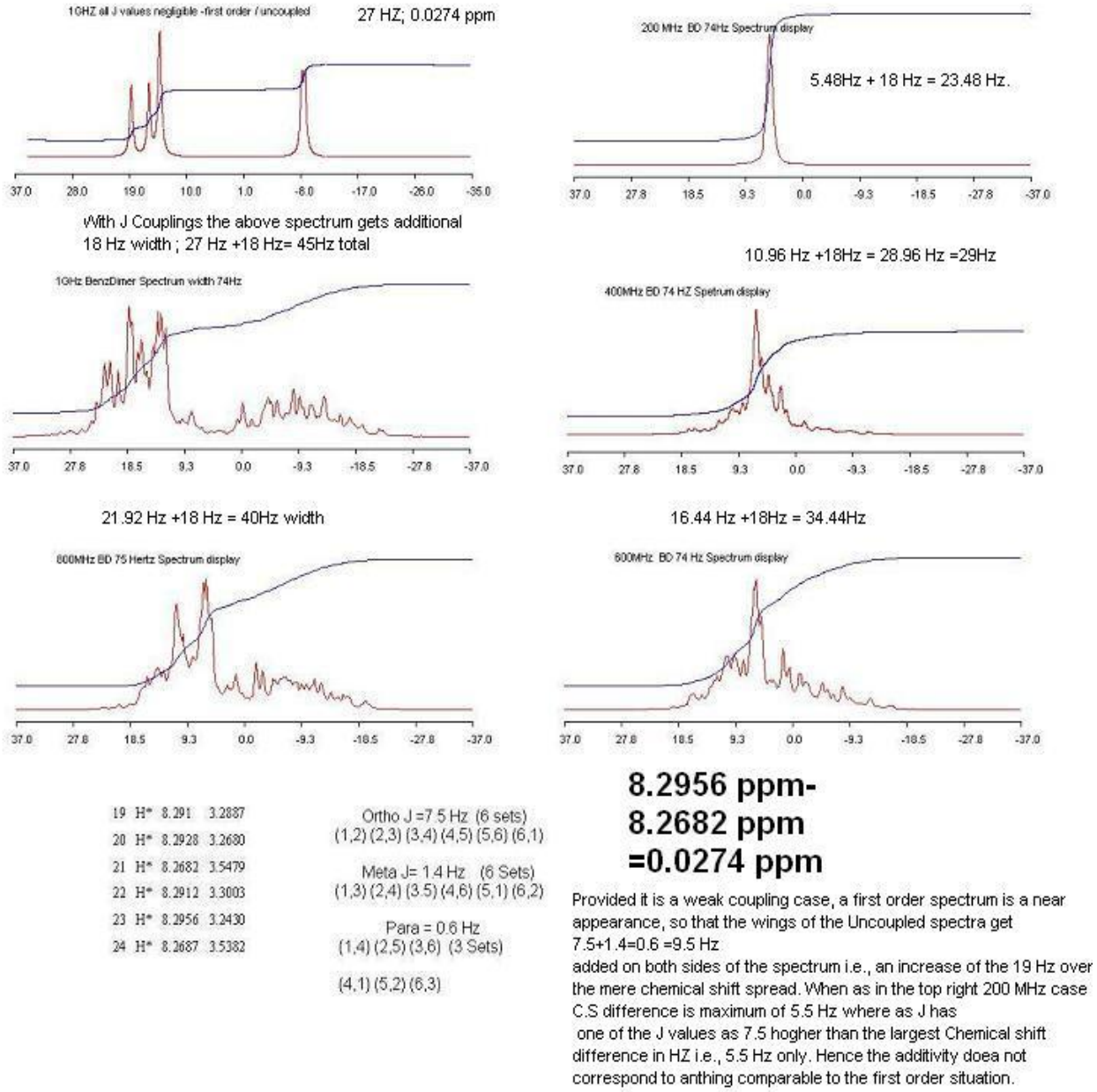

FIG.3: ***PMR simulation of BENZENE DIMER at several proton NMR frequencies (Spectrometer frequencies). The simulated spectra beyond 1GHZ is currently not possible to obtain experimentally since spectrometers are not available at these frequencies; benzene dimer itself is such an imaginary compound that it is not possible to get sample to supply for recording any spectra.***

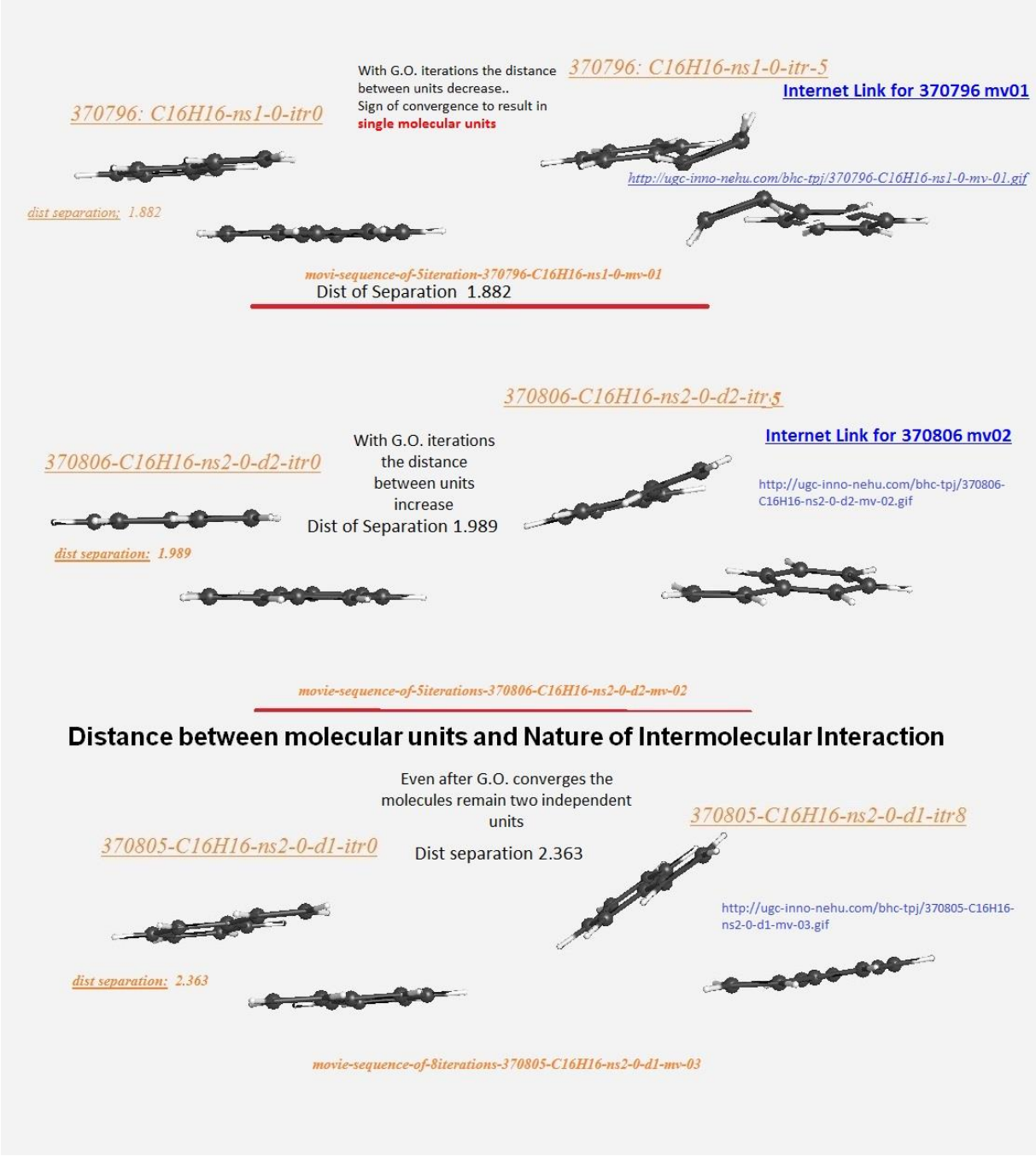

FIG.4. ***Images of the situation corresponding to visualization of iterative sequences.***

The two molecules initially placed at different distances; at a closer distance the propensity for the formation of dimer increases. These details are illustrated elaborately at reference **(4).**
The dimeric structure and the corresponding calculated NMR spectrum are depicted in FIG.5.
It could be found that the required conformation does form by such dimerization and the calculated NMR structure also resembles the experimental pattern than the other possible conformations.

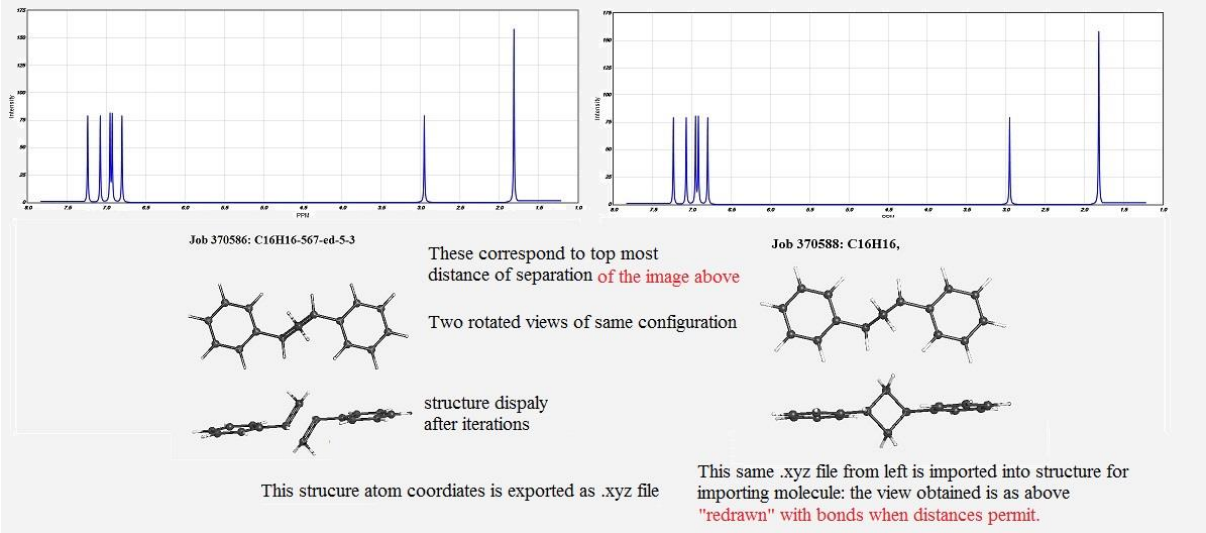

FIG.5. ***Dimer formed and PMR spectra calculated; different views of resulting dimer structure.***

3. TOPICAL APPROACH TO INCREASE EFFICIENCY OF CHEMICAL PLANT

The next illustration would be that of handling an ensemble of water molecules **(5).**

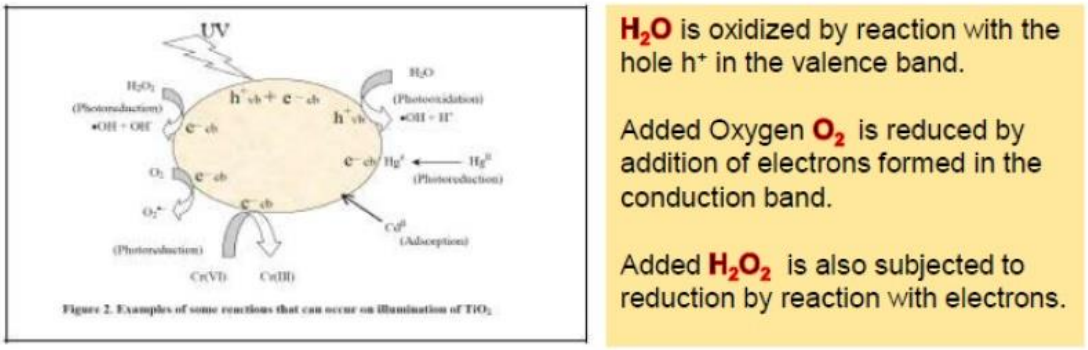

FIG.6. ***The Solid TiO_2 surface and the reactions envisaged in the polluted water medium.***

The situation is when small organic dye molecules present in industrial effluents pollute the water and by the AOP process the task is to decompose and degrade these organic pollutants. The TiO_2 semi conductor material with appropriate band gap energies can be irradiated with em radiations to produce electrons and holes. The water molecules from the bulk reach these surfaces and reacting with holes can produce radical products by splitting water and the reacrtive radicals further react with dye molecules at the surface and decompose them. The way QM studies can be made for this context is to consider the radical species, and the dye molecules together and submit the combination for QM investigation of the reaction characteristics. But the production of radical product from water in.situ at the surface of the TiO_2 and the reaction with dye molecule requires a consideration of diffusion phenomena and which is not a simple task,

For example the **FIG.7** displays a result: That 12 water molecule ensemble is considered as a molecular system to be subjected to Geometry Optimization. And, this system is attributed to have 4 -ve charges and submitted for GO.

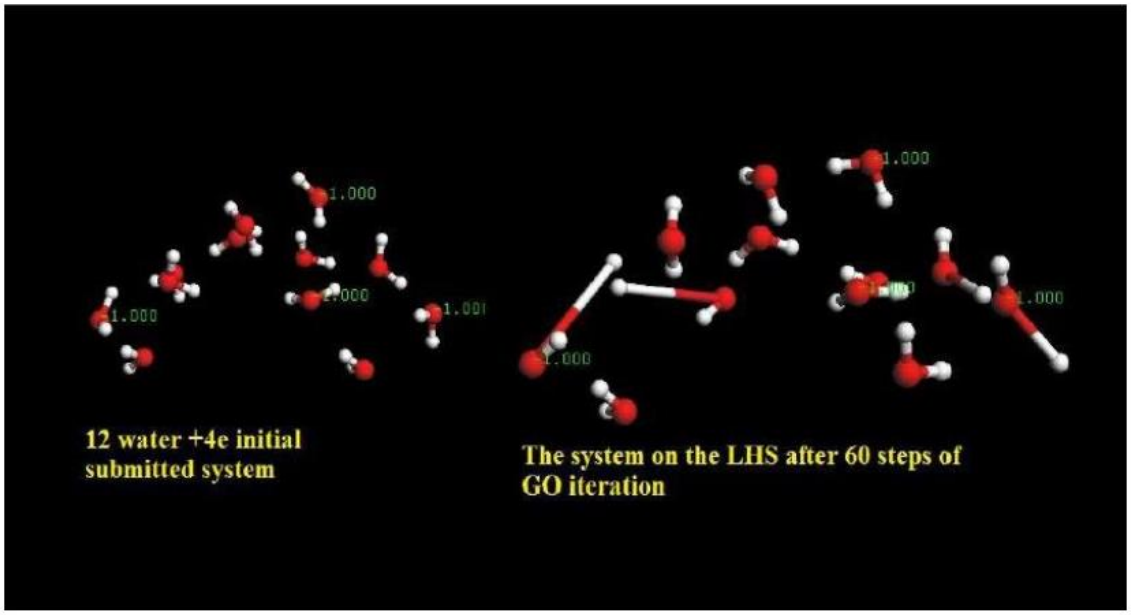

FIG.7. ***12 water molecules with +4e added is submitted for G.O. by PM3 semiempirical method at ARGUSLAB computational chemistry portal. On the RHS is the situation of this system which has gone through 60 iterative steps of GO (not yet converged).***

The situation on the RHS indicates certain molecules have one or both of their bonds elongated. It was ensured that the intermediate state when the same 12 water system is subjected to GO without adding 4e to it, this peculiarity of bond elongation does not result for the 60 steps or even till the end when the system attains 12 water attains energy minimized equilibrium distribution and GO converges. During this time interval of 60 steps, the evoloution would involve a diffusion process in water which would be rearranging the molecules. Thus at intermittent iterative steps it is necessary to stop the calculation process, edit manually based on chemical intuition and continue the iterative optimization from that stage onwards. These kind of manoeuvres seem to yield some insights as to how exactly to regulate the radical productions and reduce the radical recombination processes to increase the efficiency of AOP. These results can be appropriately translated into experimental conditions while designing water purification plants. These details as the chemists would require to know have been pointed out in reference (5).

FIG. 8. Is a situation that depicts a kind of end result as purportedly what happens in the experiments. Such studies are mostly are theoretical investigations of experimental phenomena, but till the end no comparison with experiment is required and sometimes the results when they are not the same as what experimentally thought off, then calls for additional theoretical studies, finally to be leading to novel experiments.

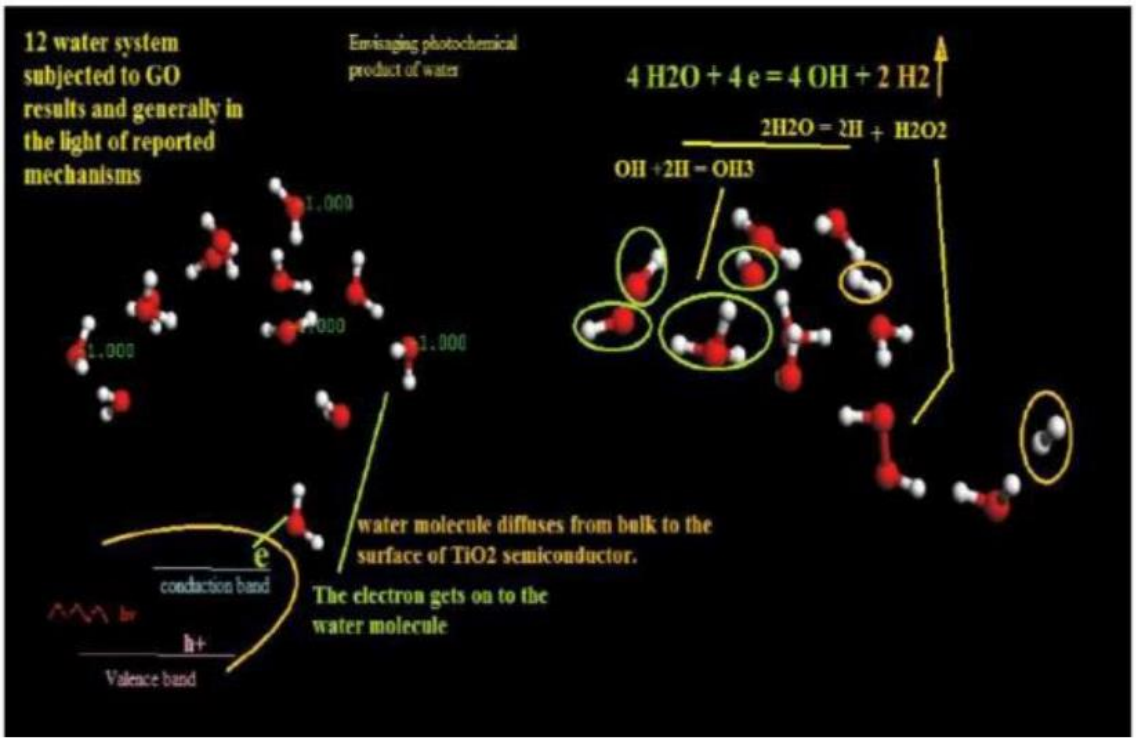

FIG.8. ***An end convergent result, similar to experimentally envisaged production of radicals, and H_2 evolutions stoichio metrically accounted. From ref (5).***

4. FOR THE INTEREST IN CHEMISTRY FROM OUT OF THE LAB INFORMATION

The next system to consider from the stand point of the theme of this paper is the combined molecular system of Methane and Benzene. This combined system (one gaseous and the other liquid in room temp) though experimentally not encountered in Chemical laboratories as any requirement for such a system, can be studied by QM abinitio methods. To consider in an elementary way, the Benzene has $\mathbf{D_{6h}}$ point group symmetry and there could be 6 bond dipole moments but net molecular dipole moment is zero. Similarly the Methane molecule ahs a Td symmetry and could have 4 bond dipoles and no net Molecular dipole moment. These molecular dipole moment situations of the two highly symmetric molecules are borne out by QM methods. However, when the two molecules with their individually optimized molecular geometry are drawn together at a distance of separation of about 5 Angstroms there is a non vanishing net dipole moment generated for the combined system and according to the calculation engine such a Dipole Moment is indicated to be located somewhere in the common region for the two molecular system. No GO is carried out only simply single point energy calculation which also calculates the net dipole moment. This raises the question as to

how Charge movement occurs to cause a net transfer of charge from one of the molecule to the other there can be net equal and opposite charge separation and a well defined dipole moment. A calculation of NMR spectrum, particularly PMR chemical shifts, results in a varied PMR pattern than the simple two line (one

benzene line at aromatic protons vale intensity 6 & one methane proton line at methane chemical shift value with intensity 4) for the non interacting systems. This study gets an elaborate treatment with more involved consideration. Obviously a Benzene+Methane system is not of much relevance to chemical study.

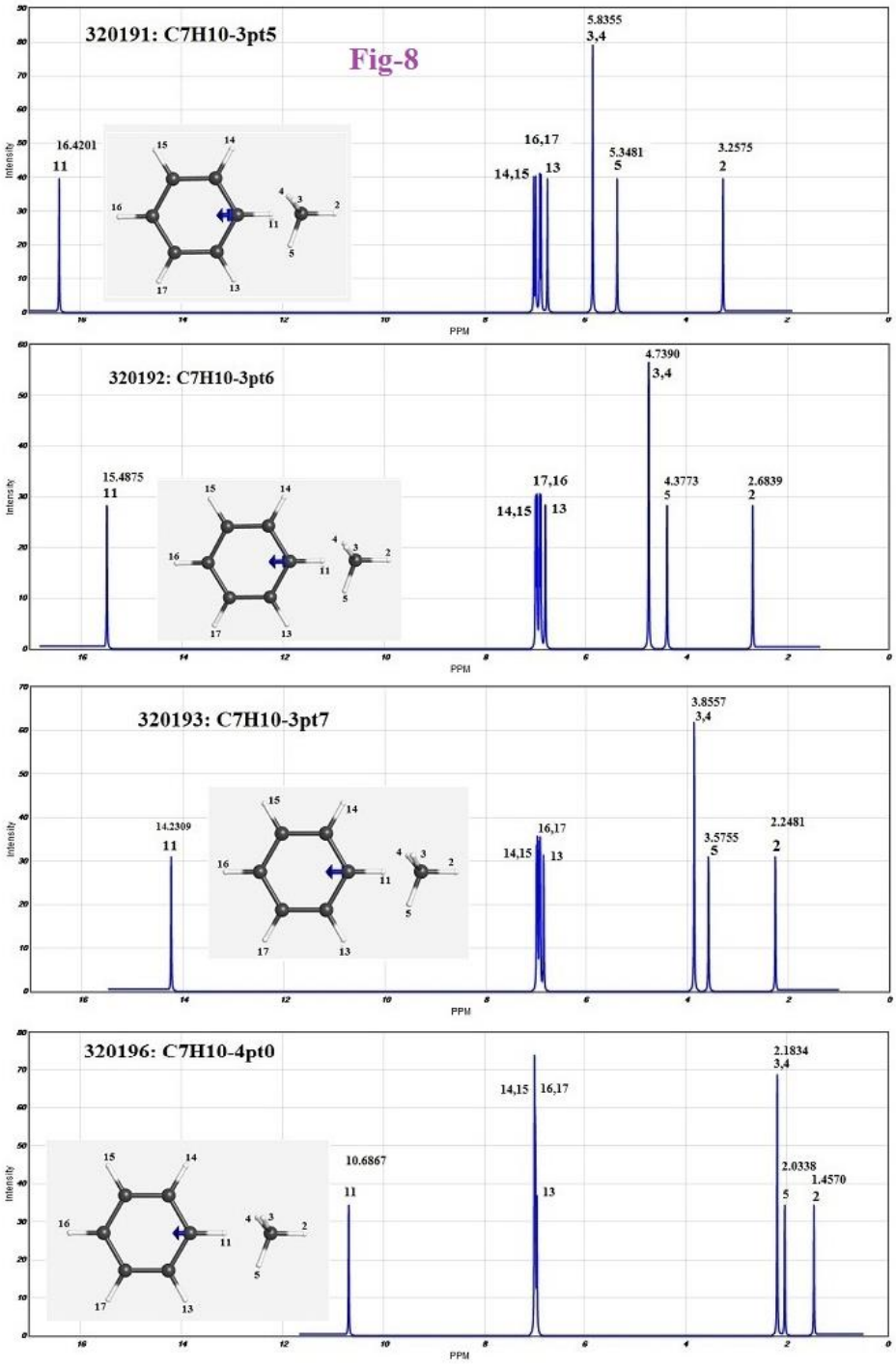

FIG 9. A typical example of the combined Methane & Benzene study, indicating net dipole moment, variation of proton NMR pattern indicating atomic charge variation merely at a farther distance compared to bond lengths.

RFERENCES:

(1) Uttamkumar Samanta, Debnath Pal and Pinak Chakrabarti, (1999), Packing of Aromatic Rings Against Tryptophan Residues in Proteins, Acta Crystallographica, Section D, D55, 1421-1427.

(2) S. Aravamudhan, (2016) personal web domain; http://www.ugc-inno-nehu.com/ This benzene dimer structure calculated NMR data at: http://ugc-inno-nehu.com/Benz2-Benz1/archive159831.tar this link archive can be imported into the www.webmo.net computational chemistry portal and results can be viewed.

(3) S. Aravamudhan, (2014), personal web documentation –internet resource. http://ugc-inno-nehu.com/saif_nehu.html at this webpage almost at the top find a hotlink Jump to **FTNMR SIMULATOR**.
Clicking on this link would let the page display jump to a link again:
File HERE **Download to Install FTNMR Simulator** from which an Fidwin.exe simulator file can be downloaded to install the simulation software in the computer. Take proper care at the instance of downloading and installing.

(4) S.Aravamudhan, (2018), Plenary lecture, Visualizing a Cycloaddition by the Abinitio SCF Methods for the formation of Polystyrene, http://www.ugc-inno-nehu.com/events-2018.html#bhc

(5) S. Aravamudhan, 2017, Studies by Computational Chemistry on the Removal of Water Pollutants using **TiO_2 /O_2/H_2O_2** Photo catalytic **AOP** Activity, Personal Webpage, Internet Resource, http://www.ugc-inno-nehu.com/events-2017.html#E09

(6) S. Arvamudhan, 2018, personal web domain content, Internet resource; Image files http://www.ugc-inno-nehu.com/ISC105-OSU/image-files/

FURTHER SUGGESTED READING:

http://ugc-inno-nehu.com/compile/07-2013-ICETCS-CUG-sa.pdf

http://ugc-inno-nehu.com/JMSE-A5-2015-p181-SA.pdf

http://ugc-inno-nehu.com/IJRDET-AugVol4Numb8-paper-sa.doc