WORKSHOP ON 100 YEARS OF THE LATIMER AND RODEBUSH PAPER ON HYDROGEN BONDING:

VOLUME 100 OF THE JOURNAL OF THE INDIAN INSTITUTE OF SCIENCE

ABSTRACT BOOK

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WELCOME

A warm welcome to everyone attending the workshop on *100 Years of the Latimer and Rodebush Paper on Hydrogen Bonding.* The weather in Bengaluru is, indeed, very pleasant during this time of the year.

By coincidence, Volume 100 of the *Journal of the Indian Institute of Science* is being published in January 2020. This Journal is perhaps unique as a multi-disciplinary review Journal. Every issue focuses on a specific topic guest edited by expert(s) and features invited review articles by several experts in the field. Realizing this coincidence, Issue 1 of the volume 100 focuses on hydrogen bonding and other intermolecular bonding that have attracted enormous interest over the last decade.

It is not an easy task to identify the person who suggested the concept of the hydrogen bonding first. Linus Pauling, who may be considered the most influential chemist from 20th century, credits the paper by Latimer and Rodebush published in 1920 as the first to mention hydrogen bonding. Pimentel and McClellan who authored the first book in this topic, titled '*The Hydrogen Bond'* start their book with a quote from this paper. However, both the book by Pauling and the paper by Latimer and Rodebush refer to previous work by Huggins at the University of California, Berkeley. A Thesis submitted by Huggins in 1919, discussing this idea, has been lost.

Pimentel and McClellan refer to the work of Nernst (1897), Werner (1903), and Moore and Winmill (1912), all of which discussed some form of hydrogen bonding between molecules. Moreover, they point out that Oddo and Puxeddu (1906) and Pfeiffer (1913) had discussed about 'intramolecular hydrogen bonding' through which two parts of the same molecule which are not directly bonded, interact through a hydrogen bond. However, what Latimer and Rodebush wrote in 1920, quoted verbatim in my article in this issue, is quite remarkable. Pimentel and McClellan wrote about this quote in their book published in 1960: *It is an amazing fact that every word of their description remains acceptable in the contexture of chemical knowledge today. But the true historical importance of this statement derives from its pioneering invasion of a frontier of chemistry that even today presents uncertain footing to the chemist.* This description remains accurate in 2020!

To mark these double centenaries, it was decided to have a workshop featuring talks by several authors and other experts. I would like to thank all the authors who contributed to this special issue of the Journal and the speakers who agreed to give a talk in the workshop. Among the Authors, we have Profs. G. R. Desiraju and S. Schenier, who have both authored popular books on hydrogen bonding. They were both members of the IUPAC task group, along with me, which came up with a new definition of hydrogen bonding in 2011. One more member from that group, Prof. A. C. Legon has contributed as well. Profs. Desiraju, Scheiner, Legon and Prof. P. Politzer were members of the IUPAC task group that defined halogen bonding in 2013 and chalcogen bonding last year.

This issue also has articles by Prof. Martin Suhm, Chairman of the Horizons in Hydrogen Bond Research Conference in 2011 at Göttingen, Germany and Prof. Josè Fernandez, who would be the Chairman of the same conference in 2021 at Bilbao, Spain. Other Authors include well established researchers who have made significant contributions to this field from India: Prof. T. N.

Guru Row, Prof. E. D. Jemmis, Prof. K. S. Viswanathan, Prof. S. J. Wategaonkar, Prof. T. Chakraborti, Prof. G. Mugesh and Prof. G. Naresh Patwari. This issue also features articles from young and accomplished researchers Prof. Himansu Biswal and Prof. Deepak Chopra. Articles cover both experimental and theoretical work in gas, liquid and solid phase.

I do realize that the issue could have had many more authors who have made important contributions to this field. Not surprisingly, I was delighted when Prof. G. K. Ananthasuresh, Editor of the Journal and Prof. Kaushal Verma, Chair of the Office of Communication suggested that we arrange a workshop focusing on this topic. Eleven of the Authors have agreed to speak in the workshop. We do have ten other speakers who have made important contributions to the field. All their abstracts are given in this booklet. My sincere thanks are due to all the authors of the issue and speakers in the workshop.

I would like to thank Prof. T. N. Guru Row (former Editor of the Journal) and Prof. G. K. Ananthasuresh for giving me the opportunity to bring out a special issue of the Journal of Indian Institute of Science celebrating 100 years of the seminal paper on hydrogen bonding. I would like to thank Prof. Kaushal Verma and Ms. Kavitha Harish from the Office of Communication for their help in organizing the workshop and also in bringing out the issue. I thank our Director Prof. Anurag Kumar and everyone in the Administration for their support in organizing the workshop. In particular, the grant from the Institute of Eminence is acknowledged. I thank Prof. CNR Rao who readily agreed to release the special issue during the workshop. I thank all the past Editors of the Journal for their participation in the function. I also acknowledge partial financial support from the SPARC project given to the Indian Institute of Science and the University of Newcastle. It is hoped that the Workshop and the Special Issue focusing on hydrogen and other similar intermolecular bonding stimulates further advances in the field.

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ARE HYDROPHOBIC INTERACTIONS DIRECTIONAL?

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Hydrophobic interaction (HI) refers to the aggregation of nonpolar moieties in an aqueous medium and it is abundant in nature only next to hydrogen bonding among non-covalent interactions. Despite its abundance, the electronic nature of HI is not firmly established in terms of directionality and interaction strength akin to hydrogen bonds and σ-hole interactions as of today. Electrospray ionization mass spectrometry (ESI-MS) measurements showed HIs between protein-hydrophobic ligand complexes are preserved in the gas phase [1,2] negating the common notion about the exclusive role of water molecules in mediating HIs between nonpolar moieties. Although there are a few computational studies on methane dimers, n-alkanes, and polyhedranes [3,4], there is no systematic experimental study of HIs such as the methyl···methyl (Me···Me) interactions in the solid state. The methyl···methyl hydrophobic interactions in a series of multicomponent crystals of biologically active molecules is quantified based on experimental charge density models using high-resolution X-ray diffraction data. The study classifies for the first time that these interactions as atypical group···group interactions in contrast to σ-hole interactions, stabilized by the minimized electrostatic repulsion and maximized dispersion forces. The solid-state entropic contribution from the torsional mode of the methyl groups in stabilizing these interactions by thermal motion analysis based on neutron diffraction as well as variable-temperature crystallography provides a quantitative estimate and is further substantiated by the appearance of a unique up field chemical shift in the ^{13}C solid-state NMR signal displayed by the carbon atoms in methyl···methyl interaction region [5].

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NOTE

THE H-BOND IN THE LINEAR ALCOHOLS IN THE LIQUID STATE: NMR MEASUREMENTS AND *AB INITIO* MOLECULAR DYNAMICS

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Quantitative information of hydrogen bonding is crucial to our understanding of the structure and properties of associated liquids. The alcohols are strongly associating liquids with hydrogen bonding associated with the presence of the hydroxyl group having a significant influence on properties. The linear mono-hydroxy alcohols, R-OH, have been considered as homologues of water where R can be varied from H to linear alkyl groups but the fact that the alcohols have both hydrophobic and hydrophilic parts makes their behavior quite different from that of water, apart from the fact that water has four potential sites for H-bonding per molecule, whereas the alcohols lack one H-bond donor site .In this talk I shall outline results from *ab initio* molecular dynamics simulations of the liquid alcohols from methanol to pentanol . From the joint radial-angular probability distribution of the intermolecular O···O distance and the HO···O angle it is possible to estimate the geometrical parameters that define the H-bond in these systems. The key feature of the H-bond in the liquid alcohols, irrespective of the size of the alkyl group, is the strong orientation dependence with the donor-acceptor HO···O angle being close to zero, a fact that we confirm by 1D Nuclear Overhauser effect measurement from the proton NMR spectra of ethanol. H-bond formation in the alcohols is consequently considered as the passage from a state where the donor-acceptor pairs show no preferred orientation, to one where they are almost linear. The potential of mean force, the reversible work associated with this process, was computed from the pair probability density distributions obtained from the simulations and that for a hypothetical state where donor-acceptors are randomly oriented. For the smaller alcohols the computed free energies for H-bond formations show the same trend as their experimental heats of vaporization.

NOTE

HYDROGEN BONDING IN DRUG DESIGN

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There has been a sea of change in our comprehension of the interactions of drugs with their target receptor/enzyme from the "magic bullets" of Ehrlich to the molecular recognition concepts today. The knowledge of the nature of these weak non-covalent forces has been used in molecular modelling of receptor-ligand interactions. A direct consequence of this knowledge is rational drug design that has increased the opportunities for new lead generation and optimisation. Hydrogen bonding is ubiquitous in the molecular recognition process in the examples that will be discussed.

NOTE

NOTHING IMPROPER ABOUT CH•••Y HYDROGEN BOND

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Although C-H···Y interactions have been recognized as H-bonding interactions for quite some time, they were not investigated spectroscopically until recently. Recent results indicated that unlike conventional hydrogen bond, C-H···Y H-bond has interesting spectroscopic characteristics, i.e., it shows both red as well as blue shift in C-H stretching frequency upon H-bond formation. I will present examples of red, blue, and zero shifted C- H···Y H-bonds investigated in our laboratory. It was found that the shift in the CH stretching frequency depends on the activation of C-H moiety. In a few instances, the C-H···Y H-bonds can provide primary or secondary stabilization for the growth of the primary solvation shell around organic molecules.

NOTE

MOLECULAR ELECTROSTATIC POTENTIAL REORGANIZATION THEORY TO DESCRIBE POSITIVE COOPERATIVITY IN NONCOVALENT TRIMER COMPLEXES

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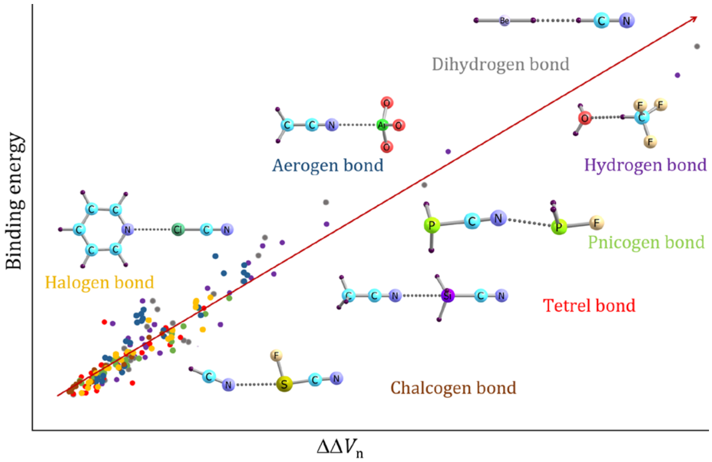
Supramolecular self-assembly and molecular recognition processes are driven mainly by positive cooperativity in noncovalent interactions. Here we report a large variety of hydrogen, tetrel, chalcogen, pnicogen, halogen, aerogen, and dihydrogen bonded dimer and trimer complexes, computed using MP2/6-311++G(d,p) level *ab initio* theory. The dimer to trimer change is associated with a positive cooperativity in all the complexes. Significant electron density reorganization occurs in monomers due to noncovalent bond formation which is quantified using the change in molecular electrostatic potential (MESP) at bonded atoms. For a noncovalent dimer X_DY_A, an electron density flow is observed from donor molecule X_D to acceptor molecule Y_A. As a result, Y_A in dimer showed a tendency to form a stronger noncovalent bond with an electron-deficient center of a third molecule while X_D in dimer showed a tendency to form a stronger noncovalent bond with an electron-rich center of a third molecule. The change in change-of-MESP at the donor and acceptor atoms involved in bond formation ($\Delta\Delta V_n$) is used as a parameter to assess the extent of electron donor-acceptor (eDA) interaction in dimers and trimers and found that $\Delta\Delta V_n$ is directly proportional to the total binding energy. A cooperativity rule is emerged from this study which states that the electron reorganization in the dimer due to eDA interaction always enhances its interactive behavior with a third molecule towards the formation of a noncovalent trimer complex.



NOTE

INTERMOLECULAR COMPLEXES AND MOLECULAR CONFORMATIONS DIRECTED BY HYDROGEN BONDS: MATRIX ISOLATION AND *AB INITIO* STUDIES

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Studies on hydrogen bonding interaction in various systems, involving phenylacetylene (PhAc), propargyl alcohol (PA), borazine (BNH), propargyl amine (PAm) were performed using matrix isolation infrared spectroscopy and supported by *ab initio* computations. Weak intermolecular interactions of the above mentioned precursors with water, methanol, ether, acetylene and benzene were studied. These systems manifested O-H…π and n-σ* interactions, such as C-H…O, N-H…O, O-H…O and O-H…N. In several cases the complexes were multiply tethered involving two or more of the above mentioned contacts. Many of the weak complexes exhibited a number of isomers, and the relative importance of the multiple non-covalent contacts resulted in a competition between the various isomers for the global minimum. It was found that subtle changes in the structures of the precursors tilted the balance towards one isomer or the other. Our studies also threw up a systematic method of building possible structures for complex systems starting from the known structures of related simple systems. We also studied the homodimers of PA and BNH. The BNH dimer was particularly interesting as one of its isomers was characterized by a bis-dihydrogen bond. We also studied the influence of hydrogen bonding interactions in determining the conformational landscape and preference in amino acids. Here again we were able to draw some generalizations regarding the conformational stability of amino acids. The combination of matrix isolation and *ab initio* computation is a powerful tool for studies on weak intermolecular interactions and conformations.

NOTE

NEWLY IDENTIFIED WEAK INTERACTIONS IN PROTEINS – SOME COULD TURN OUT TO BE DESTABILIZING

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Macromolecules are characterized by typical arrangement of various non-covalent interactions. In a typical N−H···N interaction observed in DNA and protein, the N−H direction is coplanar with the ring moiety containing the acceptor N atom. In contrast, the interaction could also be in a perpendicular orientation, which we designate as N−H···N(p_z) interaction. This interaction was found to form fused five-membered rings motif (involving two consecutive residues), and two such motifs from distant region in the protein sequence could be linked together through hydrogen bonding to form what we termed as *topi* (because of its shape like a hat). Remarkably, *topi* is found within disease causing misfolded proteins, such as fibrilled form Aβ42. The N−H···N(p_z) interaction was also identified in another three-residue motif, which was shown to be a variant of inverse γ-turn.

The local structure of the disulfide bond (Met, as well) is known to be stabilized through S···O interactions, akin to what takes place between an electrophile and a nucleophile during organic reactions. Some of the specific impairments inflicted upon highly brilliant X-ray irradiation (during data collection on protein crystals) are disulfide bond cleavage. However, all disulfide bridges are not equally susceptible to damage. Consideration of the disulfide bonds in the structures of elastase, lysozyme and acetylcholinesterase indicate that the S-S bonds which have a close contact with a carbonyl oxygen atom along the extension of the bond are more susceptible to breakage. Such geometry provides a pathway of electron transfer to the S-S bond leading to its reduction during exposure of the protein crystal to intense X-ray beam. Thus an interaction that is stabilizing per se causes a loss of integrity of disulfide bond on Xray exposure.

NOTE

CARBONYL-CARBONYL $n_N \rightarrow \pi^*$ AND n_N (AMIDE) $\rightarrow \pi^*/\sigma^*$ INTERACTIONS IN SMALL MOLECULES, PEPTIDES AND PEPTIDOMIMETICS

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The carbonyl group is ubiquitous in both chemistry and biology. Apart from being involved in numerous chemical transformations, the carbonyl group also participates in various distinct weak noncovalent interactions including hydrogen bonding (C=O···H-X)[1], carbonyl-chalcogen interactions (C=O···X; X = S, Se, Te)[2] and nucleophile-carbonyl interactions (Nu···C=O)[3] . In recent years, carbonyl-carbonyl (CO···CO) interaction[4] has emerged as an important weak interaction due to its ability to stabilize both small- and macromolecules including peptides and proteins.[5] The CO···CO interaction is believed to be n → π* in nature wherein the lone pair of the oxygen atom of a carbonyl group is delocalized over the π* orbital of the C=O bond of another nearby carbonyl group. Recently, we discovered the "reciprocal" variant of CO···CO interaction in small molecules and proteins, especially in PPII helices.[6a] We have also shown the scope of utilizing this interaction as a means to impart structural rigidity in drug-like small molecules.[6b] Our recent investigations revealed that there are at least six different ways in which two carbonyl groups can engage in CO···CO interactions of which only two have been observed in proteins so far.[6c] In this talk, I will discuss our current understanding of CO···CO interactions with a focus on the "reciprocal" variant. I will also discuss about our recent discovery of an unusual n_N (amide) → π*/σ* interactions in the stabilization of N,N'-diacylhydrazines.

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NOTE

HALOGEN BONDING IN THYROID HORMONE ACTION AND MEMBRANE TRANSPORT

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Thyroid hormones regulate almost every process in the body, including body temperature, growth, and heart rate. They influence carbohydrate metabolism, protein synthesis and breakdown, and cardiovascular, renal, and brain function. The deiodination of thyroxine (T4) by iodothyronine deiodinases (DIOs) play a crucial role in thyroid hormone action. These enzymes contain selenocysteine, the 21st amino acid, in their active sites. The phenolic ring (5′) deiodination of T4 by the type 1 and 2 enzymes (DIO1 and DIO2) produces the biologically active hormone, 3,5,3′-triiodothyronine (T3), whereas the tyrosyl ring (5) deiodination of T4 by the type 3 enzyme (DIO3) produces the biologically less active hormone rT3. Therefore, the complex biochemical dehalogenation pathways play an important role not only in human hormone action, but also in the development of drugs for thyroid-related disorders.

In this lecture, the chemical mechanism by which the deiodinases and organoselenium compounds selectively activate and inactivate the thyroid hormones will be discussed. The role of iodine atom, halogen bonding and endosomolytic peptides in the membrane transport of fluorescent molecules will also be discussed.

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NOTE

DECIPHERING THE NATURE OF UNCONVENTIONAL HYDROGEN-BONDS FROM IR SPECTROSCOPY DATA

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Hydrogen-bond, in spite of being a century old concept, is still one of the most enthralling topics of research in the scientific community. Conventional hydrogen bond is generally denoted by X-H…Y where both X and Y are electronegative atoms. However, the recent redefinition of the hydrogen bonding by the IUPAC committee goes beyond the conventional wisdom on this non-covalent interaction.[1] Consequently, there has been a growing search for finding the presence of this ever interesting non-bonded interaction considering various atoms in the periodic table as hydrogen-bond donor (X-H) and acceptor (Y). We have studied various types of hydrogen-bonds involving either the hydrogen-bond acceptor as a weak electronegative atom or both the hydrogen-bond donor and acceptor atoms as weak electronegative atoms. Specifically, we have explored N-H…Se hydrogen-bond by studying indole…dimethyl selenide complex[2-3] as well as S-H…S and S-H…Se hydrogen-bonds[4] by studying 2-chorlothiophenol…dimethyl sulphide and 2-chorlothiophenol…dimethyl selenide complexes, respectively, using resonant 2-photon ionization (R2PI), IR-UV double resonance spectroscopy and quantum chemistry calculations. We have observed that the IR red-shift values of the N-H stretching frequency in the N-H…Se hydrogen-bond and the S-H stretching frequency of the S-H…S and S-H…Se hydrogen-bonds are similar to those in any conventional hydrogen-bond in spite of the presence of relatively smaller amount of electrostatic component in the former ones. Energy decomposition analysis of these hydrogen-bonded complexes as well as frontier molecular orbital calculations indicate that the Charge transfer/Orbital interaction plays a significant role for the large red-shifts observed for these unusually strong hydrogen-bonds.

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NOTE

NMR METHODOLOGIES FOR THE INVESTIGATION OF HYDROGEN BOND

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The rare examples of intramolecular hydrogen bonds of the type the N–H---F–C have been detected by utilizing multinuclear and multidimensional NMR techniques, in number of synthesized molecules containing organic fluorine. The detection of through-space couplings, such as, $^{1h}J_{FH}$, and $^{1h}J_{FN}$ of substantial strengths and feeble structural fluctuations as a function of site-specific substitution of fluorine atoms within the basic identical molecular framework provided direct evidence for the existence of intra-molecular HB. The transfer of spin polarization between interacting spins through hydrogen bond is established by perturbing their strengths and monitoring their influence on NMR parameters. The selective and non-selective excitation and detection of forbidden Nth quantum coherence of N scalar coupled heteronuclear spins, an unconventional NMR, has been employed both for spin system filtering and for the determination of the relative signs of through space and through bond couplings, which are crucial for establishing the existence of hydrogen bond.

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NOTE

CONTINUUM IN H-BOND AND OTHER WEAK INTERACTIONS (X-Z…Y): SHIFT IN X-Z STRETCH FROM BLUE THROUGH ZERO TO RED.

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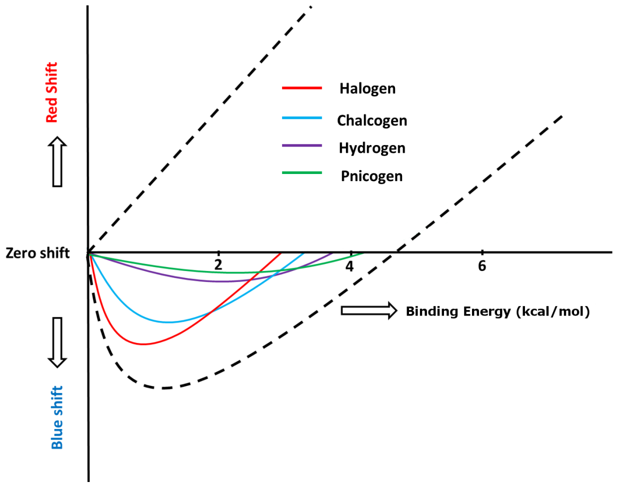
Variation of X-Z stretching frequency in the formation of Z-bonds (XZ…Y, Z=H, or other main group element) is reviewed. Majority of hydrogen bonds (H-bonds) occur between a strongly polar X-H bond and an electron pair donor (H-bond acceptor) Y and show a red shift in the X-H stretch. In very weak H-bonds there are several instances where the X-H bond is blue-shifted. We show that X-H shifts span a continuum going from red through zero to blue; there is nothing improper or anti about H-bonds that are blue-shifted. Other Z-bonds bring more factors in deciding the blue and red shift. In general when negative hyperconjugation in the monomer X-Z outweighs the charge transfer from incoming electron rich species Y during the formation of X-Z…Y (Z = halogen, chalcogen etc), it leads to blue shifting X-Z bond. In the absence of negative hyperconjugation in the monomer, elongation of X-Z bond length (red shift) is almost always observed on complexation with Y. In an X-Z…Y interaction, the nature of X has the major influence on the way, Z and Y control bond length elongation/contraction. It is possible to show using carefully selected examples that the continuum of bonding extends to the whole range of bonding in chemistry.



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NOTE

INFLUENCE OF H-BOND IN THE CHARGE TRANSFER DYNAMICS

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Understanding charge transfer (CT) across hydrogen bonds is of fundamental importance in elucidating important chemical/biochemical process in a diverse number of systems, starting from simple molecule to complicated natural enzymes, proteins and DNA. Unlike covalent bonds, hydrogen-bonding interactions are predominantly electrostatic in nature. The H atom present at the centre of three linear atoms D-H…A in H-bonding network makes it relatively weak, flexible, and dynamic. The process of transferring electron across this intermolecular interface has long inspired explorations for theoretical chemist, where many models have been proposed. This work highlights microscopic mechanisms of CT in hydrogen bonded molecular and crystalline systems. Few synthetic analogous of the peptides and imidazolinium based ion pairs have been considered as an example to explore the efficiency of the CT through H-bond.

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NOTE

HYDROGEN BONDS BETWEEN SAME CHARGE SPECIES: INSIGHTS FORM COMPUTATIONAL STUDIES.

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Interaction between same charge species such as, cation···cation or anion···anion is destabilizing due to large Columbic repulsion observed between the two ions. Recent literature reports several examples of the occurrence of associated same charge species held by intermolecular interactions such as, hydrogen bonds.[1] Hydrogen bonds in these cases has been called pseudo, anti-electrostatic and destabilizing types.[2] Moreover, the occurrence of short hydrogen bonds between cation···cation or anion···anion in the crystals is proposed to be a results of Columbic compression caused by counterions.[3] We recently observed several cation···cation species held together by hydrogen bonds of the type N–H···O, O–H···O and C–H···O in the crystalline salts forms of a nutraceutical compound synephrine.[4] We studied the observed molecular cationic pairs with the help of various theoretical approaches. The results obtained by us were in contradiction with the earlier assumptions that consider such hydrogen bond as destabilizing. We observed no significant difference in the molecular geometry and the stability imparted by cation···cation hydrogen bonds in crystalline environment (under columbic compression) and the gas phase (free from counterions). Over study provides new insights into the nature and strength of the hydrogen bonds present between the cationic molecular pairs and helps in delineating the role of hydrogen bonds in providing stability to the molecular assembly.

Acknowledgements

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NOTE

HYDROGEN BONDING EFFECTS ON PHOTOCHEMISTRY AND VIBRATIONAL DYNAMICS IN SELECTED BINARY MOLECULAR COMPLEXES

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In my talk, I shall present an overview with selected illustrations of the experimental studies performed recently in our laboratory demonstrating the role of hydrogen bonding as a driving force for specific reaction channels in some binary molecular complexes, and also as a promotional factor in intermolecular vibrational energy relaxations. The complexes were prepared under supersonic jet expansion and also under matrix isolation conditions, and vibrational and electronic spectroscopic methods were used to probe the reactions as well as the signatures of vibrational dynamics. The light absorbing chromophoric moieties used are of two types, 7-azaindole and phenol derivatives, and pure and mixed binary complexes prepared involved O-H···O, O-H···N and N-H···N types hydrogen bonded linkages. The promotional effect of vibrational relaxation has been demonstrated showing large broadening of either of the infrared X-H stretching fundamentals in X-H···Y H-bonded networks, or unusual broadening of the fluorescence spectra upon excitations to single vibronic levels of the H-bonded complexes. Light-induced HF elimination from the H-bonded dimers of fluorophenols have been used to demonstrate how H-bonding initiate the reaction channel that does not occur in monomer, and also how the reaction yields are enhanced.

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NOTE

EXPLORING HYDROGEN BONDING IN GAS PHASE MOLECULAR COMPLEXES BY BROADBAND ROTATIONAL SPECTROSCOPY

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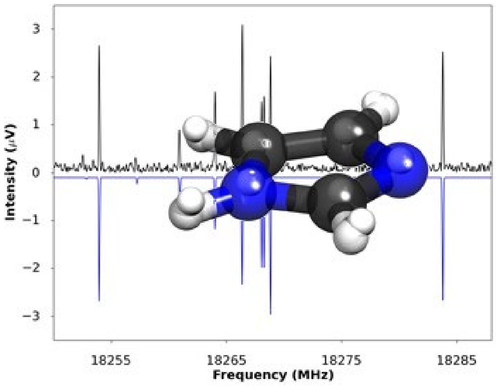
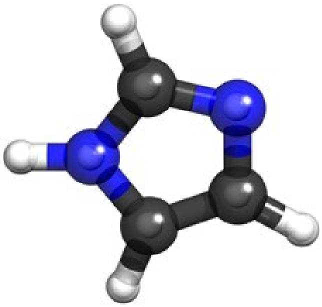
Rotational spectroscopy provides unrivalled precision for the determination of molecular structure in isolated, gas phase species. Electronics capable of digitising waveforms at gigahertz frequencies now allows chirped-pulse Fourier transform microwave spectroscopy to be performed at high resolution, high bandwidth and with minimal or no cost to sensitivity. The focus of this presentation will be recent experiments to study hydrogen bonds in complexes containing imidazole ($C_3N_2H_4$) or methylimidazole ($C_4N_2H_7$). An imidazole dimer has been identified and characterised by its microwave spectrum. This dimer is held together by a hydrogen bond between the pyrrolic hydrogen of one imidazole monomer and the pyridinic site on another. It will be shown that two isomers of a complex formed of H_2O and $C_3N_2H_4$ can be isolated and observed within a supersonic jet. Water can act as hydrogen bond donor at the pyridinic site of imidazole to yield a comparatively rigid complex. In contrast, the attachment of H_2O at the pyrrolic site of imidazole yields a complex characterised by large amplitude motions. Barriers to internal rotation of the CH_3 group on each of N-, 2-, 4- and 5-methylimidazole have been determined and shown to depend on the symmetry of electronic orbitals on CH_3 and the aromatic ring. Work in progress is exploring how the attachment of H_2O to methylimidazole affects the relative magnitudes of these barriers.





NOTE

UNRAVELLING THE SIGNIFICANCE OF HALOGEN BASED INTERMOLECULAR INTERACTIONS IN CRYSTALLINE BENZAMIDES

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Halogenated organic molecules have received considerable attention in natural sciences (*) with applications in medicines and material applications [1-2]. For an improved understanding of the chemical and physical properties of these halogenated molecules, a systematic investigation of various intermolecular interactions involving halogens is important. The halogens which are directly connected to the aromatic ring are involved in a variety of non covalent interactions, e.g. C–H…X hydrogen bonds [3], X…X interactions [4] and C–X…π interactions [5].

In this regard, we have undertaken to systematically perform a quantitative analysis of the different interactions in halogenated benzamides involving the CF_3 group. A total of 23 such molecules were synthesized and characterized using single-crystal X-ray diffraction. The influences of Cl/Br/I and trifluoromethyl substituents on the respective interactions were examined in the presence of a strong N–H…O hydrogen bond. This exercise has resulted in the documentation of frequently occurring supramolecular synthons, involving halogen atoms, in the crystal packing of benzamide molecules in the solid state. In the present study, a detailed quantitative evaluation has been performed on the nature, electrostatic contributions, and topological properties of short and directional intermolecular interactions derived from the electron density on halogenated benzamides in the solid state. A ‘region of co-existence’ involving different interactions in various structural motifs in the vicinity of the sum of the van der Waals radii has been identified [6]. Thus, the nature of the halogen (effective size), type of interaction and the packing characteristics via presence of additional interactions establish the subtle, yet important, role of cooperativity in intermolecular interactions in crystal packing.

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NOTE

EXPLORING THE STRUCTURAL LANDSCAPE OF XENO NUCLEIC ACIDS

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The evolutionary selection of the canonical nucleobases that constitute DNA and RNA has been subject of debate. Several variants have synthetically modified nucleic acids, which differ in the composition either of nucleobases or sugar or the phosphate group relative to the canonical structures have been reported.[1] Kool and co-workers have shown that DNA polymerases can replicate with high efficiency nonpolar isosteric base analogues and inferred that DNA polymerases have shape preference over Watson-Crick base pairing.[2] The structural landscape of xeno nucleic acids was explored in two independent set of studies. The mass selected infrared spectroscopic measurements suggest that the N-heterocyclic aromatic rings prefer π-stacking over other modes of the intermolecular interaction, when the number of nitrogen atoms in the ring are two or more.[3] Further, using molecular dynamics simulations it was shown that stereochemistry at the C3' position in furanose ring determines the helicity in double-stranded nucleic acids.[4]

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NOTE

SUPERCOOLING AND FREEZING OF WATER DROPLETS EVAPORATING IN A VACUUM

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A liquid in a vacuum is subject to rapid evaporation causing extremely fast cooling. The present study answers naive questions: how fast and at what temperature does water get frozen in a vacuum? Although it has been a challenge to perform such experiment due to difficulties in introducing water into a vacuum under its high vapor pressure, a few attempts have been made recently [1,2]. Here we present our own approach to generate a size-controlled water droplet on demand in a vacuum [3]. The evaporative cooling process is characterized by experiment and numerical simulation.

A water droplet with a diameter of 50−70 μm is produced by a piezo-driven droplet nozzle. The exit of the nozzle is placed in a vacuum chamber to generate a droplet directly into a vacuum. We found that it is crucial to evacuate a liquid reservoir as well to prevent water from being pressurized to flow into the vacuum chamber continuously. The droplet was illuminated either by a strobe LED to evaluate its size as a function of time or by a laser beam for depolarization measurement to probe liquid-to-solid phase transition, where droplet images were captured by a CMOS camera through a microscope lens system.

A fraction of frozen droplets (a freezing curve) was measured as a function of time up to 11 ms by examining 200 water droplets at each time. On the other hand, temporal evolution of the droplet temperature (a cooling curve) was simulated based on thermodynamic data such as heat capacity, vapor pressure, etc. It was revealed by combining the experiment with the simulation that the water droplets are frozen within 10 ms after generation at a deeply supercooled temperature between 233 and 236 K. Further simulation of the freezing curve allowed us to suggest reliable data for temperature-dependent homogeneous nucleation rate that is in debate. These studies would contribute to characterizing hydrogen bonding of water in a supercooled state as observed by X-ray diffraction [1] or by Raman scattering [2].

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NOTE

HYDROGEN BONDS WITH SULFUR AND SELENIUM: A JOURNEY FROM FOUR-ATOM DIMER TO FOURTEEN-KDA PROTEIN

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The last decade has seen several discoveries of noncovalent supramolecular forces such as tetrel bonding[1], pnicogen bonding[2], chalcogen bonding[3], halogen bonding[4] and aerogen bonding[5] and last but not least the hydrogen bonds with sulfur and selenium. These interactions are essential to understand the supramolecular chemistry and biomolecular structures.[6] In this talk I shall present recent developments and our contributions in this research area, explaining the existences and general consensus and counter intuition about sulfur and selenium centered hydrogen bonds.[7-10] A brief overview of the experimental techniques and computational methods employed to understand such hydrogen bonds present in four-atom H_2S dimer to fourteen-kDa ferredoxin will also be discussed.

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NOTE

LATIMER AND RODEBUSH (1920) AND SHAMA RAO AND JATKAR (1943) AND TODAY: HYDROGEN BONDING CONTINUES TO BE AN ELEPHANT

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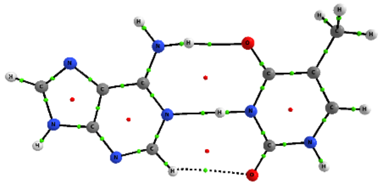
In the year 1920, Wendell M. Latimer and Worth H. Rodebush published a paper[1] in the *Journal of the American Chemical Society* titled "*Polarity and Ionization from the Standpoint of the Lewis Theory of Valence*". In this paper, they proposed that in liquid water, *"a free pair of electrons from one water molecule might be able to exert sufficient force on a hydrogen held by a pair of electrons on another water molecule to bind the two molecules together"*. Pauling[2] credits this paper as the first to mention hydrogen bond and concluded that *"the hydrogen bond is largely ionic in character, and that it is formed only between the most electronegative atoms"*. Pauling had concluded that only when X in XH is F/O/N, hydrogen bonding would be possible. In 1943, Nagamani Shama Rao and S. K. K. Jatkar[3] published a paper in the *Journal of the Indian Institute of Science* titled *'Hydrogen Bond in Benzene'*. In this paper, based on bulk properties of associated liquids, they had concluded that C-H group in benzene can form a hydrogen bond. They also pointed out that methane hydrate, which was considered to be bound by van der Waals forces, could really be bound by hydrogen bonds, *'if the hydrogen bond is given the property of the co-ordinate link'*. This statement can very well define the progress in hydrogen bond research. Throughout the century that followed the Latimer and Rodebush paper, scientists have worried about whether a specific interaction involving the H from an XH group is hydrogen bonding or van der Waals interaction. The structure of A-T base pair is widely considered to have two hydrogen bonds and a third C-H···O contact is being debated as to whether it is a hydrogen bond or van der Waals contact. This talk will summarize the two papers and more recent results, as given in my paper[4] in the Special issue of the Journal of the Indian Institute of Science, Volume 100, issue 1.



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