

# Report for the second year for the project NSC96-2113-M-009-022-MY3 (Theoretical Modeling of Carbon Nanostructures)

**Principal investigator:** Henryk Witek, Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu

The main topic of the current scientific investigations in our group is the analysis of structure and various physical properties of simple and advanced molecular aggregates consisting mainly of carbon atoms. This group of systems includes not only simple carbon nanostructures, like fullerenes and nanotubes, but also their various complexes, large hydrocarbons, and various conjugated polymers. In recent years a large number of new interesting and fascinating forms of carbon-containing molecules and structures have been found. The reported structures have been mostly observed in experiment, leaving vast space for speculations regarding the mechanism of their emerging and decomposition, and also raising numerous issues about their stability and their various molecular properties. A theoretical assistance in computer-aided simulations of these carbon nanostructures is not easy since in most cases they contain a large number of atoms and at the same time require quantum treatment. The aforementioned theoretical analysis of the physical and structural properties of the carbon nanostructures is performed using the self-consistent-charge density-functional tight-binding (SCC-DFTB) method, which has been developed for a number of years in our and our collaborators laboratories. SCC-DFTB constitutes a perfect theoretical tool that can provide answers to multiple questions posed by experimentalists. We believe that our studies can closely assist the experimental investigation of carbon nanostructures and help to uncover the theoretical mechanisms and principles underlying their chemistry and physics.

One of the most important topics pursued in the second year of the NSC96-2113-M-009-022-MY3 project was investigation of the evolution of various physical properties of  $\pi$ -conjugated oligomers with the increasing length of the system [Ref.9]. In the limit of an infinite chain, the studied systems converge toward polymers. Thus, it would be natural to think that also the properties of the finite oligomers should converge toward those of the polymers. This concept is a foundation of so-called "oligomer approach" used for experimental and theoretical determination of properties of infinite polymers. A

natural, theoretical alternative to the oligomer approach are the usual techniques of solid-state physics dealing with infinite systems and the translational symmetry. Both of these methodologies were used in a number of studies to investigate a variety of physical properties of extended systems. However, none of these publications was fully devoted to a systematic analysis of the rate of convergence of the aforementioned properties of finite molecules upon elongation toward the values characteristic for the corresponding infinite systems. Such practical knowledge would certainly simplify the studies of polymers based on the oligomer approach. At present, one has to investigate a series of homologues—some of them very far from the convergence region and some of them already beyond the saturation limit—to get the information about the properties of polymers. This makes the oligomer approach, theoretical or experimental, unnecessarily expensive and cumbersome. Thus, a methodical determination of the convergence region for various oligomer properties would make such studies much more automatic and efficient.

We have investigated the behavior of various geometrical and electronic properties of a series of structurally-related  $\pi$ -conjugated oligomers in their ground electronic states. We explicitly consider oligomers built of the following trans-connected monomers: cis-1,3-butadiene, cyclopentadiene, pyrrole, furan, and thiophene. In principle, two mesomeric forms are possible for the studied systems, aromatic and quinoid (or trans-cisoid and cis-transoid, respectively), which differ by the relative position of double bonds in the carbon backbone. Since it was demonstrated that the former form is substantially lower in energy, we consider only the aromatic-like oligomers and polymers. Note that the resulting infinite structure obtained from cis-1,3-butadiene is distinct from that one of all-trans-cisoid polyacetylene that was studied previously. We focus on the rate of convergence of the following physical properties: equilibrium structures, HOMO-LUMO energy gaps, electronic densities of states, distributions of induced charges, dipole and quadrupole moments, and polarizabilities. Our main interest lies in determining how rapidly the aforementioned properties saturate towards a constant value in the interior of the oligomers. Also, we want to find out the minimum length of the oligomer chain for which the properties are indistinguishable from those of a given polymer. Selected properties of the systems studied by us were already investigated either theoretically or experimentally in a number of studies.

The theoretical tool used for our analysis is based on the self-consistent-charge density-functional tight-binding (SCC-DFTB) approximation, which can be considered as a simplified version of density functional theory (DFT). We are fully aware that the results obtained within the framework of this method may not be very accurate. In fact, quantitative assessment of some of the studied properties, e.g., polarizability or quadrupole moment, is known to require highly advanced theoretical techniques and large basis sets. However, we are interested in the evolution of the physical properties rather than in their actual values. We are convinced that the qualitative picture we have obtained is correct even if the quantitative accuracy may need further verification by more elaborate theoretical treatment. On the other hand, using SCC-DFTB gives us the advantage of investigating extended molecular systems necessary to study the evolution of properties, which converge only in the limit of very large oligomers containing hundreds of atoms. An argument in favor of using SCC-DFTB for the analysis of  $\pi$ -conjugated systems is the successful application of this method in studying analogous properties of finite and infinite linear carbon chains. A comparison with experimental and more advanced theoretical results demonstrated an excellent performance of the approximate approach. Another very important advantage of using the SCC-DFTB method for our investigation is the possibility of a direct comparison with the analogous solid-state results. It should be stressed that the same identical SCC-DFTB Hamiltonian is used within the usually incompatible frameworks of quantum chemical and solid-state machineries. For the studied evolution of physical properties in oligomers, the solid-state calculations provide us with the necessary benchmark of relevant values for infinite polymers.

The practical applicability of our results is not limited only to the methodological issues. The conclusions obtained from our investigations can be directly applied for studying various properties of conducting polymers, which have stimulated widespread attention since Shirakawa's discovery of highly conductive polyacetylenes. The conjugated polymers are widely applied to fabricate light emitting diodes (LED), biosensors, photovoltaic cells, etc. The first five-member heterocyclic polymers studied in detail were polypyrrole and polythiophene. Polypyrrole was found to be an insulator with a band gap of 2.85 eV. However, after oxidative doping its conductivity reached 500 S/cm. Polythiophene was also found to be an insulator with a slightly smaller band gap of 2.0 eV, and the conductivity of 2000 S/cm was reported for its doped derivatives.

Later, a successful synthesis of polyfuran, with a band gap of 2.35 eV and conductivity of 100 S/cm (in a doped form), was reported. Polycyclopentadiene has been studied only theoretically. The smallest computed band gap is 0.98 eV (extrapolated TD-DFT/B3LYP oligomer results). Eventually, trans-cis-polyacetylene, which can be treated as the carbon skeleton of all of the previously discussed systems, was studied theoretically as a less stable isomer of all-trans-polyacetylene. The presence conjugated  $\pi$ -electron system results also in increased dependence of polarizabilities and second-order hyperpolarizabilities on details of the molecular structure, which opens the way of engineering the molecular properties so that they can be used in various photonic devices like optical switches, logical gates or signal processors.

Understanding large carbon aggregates very often requires understanding their simple systems and actually very complicated physical mechanisms describing their electronic structure. Therefore, in [Ref.7] we study also some small aggregates of carbon atoms. This study is focused on explaining vibrational signatures of the  $C_5H$  radical. Experimental measurement of various IR hydrocarbons signals in solid neon matrices revealed presence of linear  $C_5H$  radical. The experimental assignment has been corroborated by accurate calculations of fundamental vibrational wavenumbers of gaseous  $C_5H$ . For this purpose, we have employed the electron-attachment equation-of-motion coupled-cluster technique (EOMEA-EOMCC) and the correlation-consistent polarized-valence double-zeta (cc-pVDZ) basis set of Dunning. The fundamental wavenumbers have been computed using second-order perturbation theory from an initial harmonic-oscillator rigid-rotor approximation. An accurate theoretical determination of the fundamental  $\sigma^+$  wavenumbers is crucial for a validation of our experimental assignment, because the commonly reported harmonic wavenumbers, bearing an error 100-200  $cm^{-1}$ , give little information on the identity of the analyzed species in the spectrally congested region above 3000  $cm^{-1}$ . The calculations have been performed with the CFOUR program (CFOUR). We considered explicitly three isotopically substituted species –  $C_5H$ ,  $C_5D$ , and  $^{13}C_5H$ , which correspond directly to the species observed in our experiments. The mean absolute deviation between the corresponding computed and measured fundamental  $\sigma^+$  wavenumbers of  $C_5H$  (and its isotopic variants) is 28  $cm^{-1}$ . This agreement is deemed entirely satisfactory when one takes into account that the experiment is performed in a solid neon matrix whereas the calculations pertain to an isolated molecule as in the gaseous phase. In general, the solid neon matrix shift is

expected to be within  $\pm 1\%$  of the fundamental value, which correlates satisfactorily with the slightly larger discrepancies observed for the carbon-hydrogen stretching wavenumbers. These deviations might be decreased on employing a larger basis set in the calculations, but the resulting theoretical framework would be expensive. Another, and potentially much more important, source of the observed discrepancy can be the Renner-Teller effect expected for  $C_5H$ , a typical linear system with a degenerate electronic ground state. We observed a manifestation of this effect during our calculations of anharmonic wavenumbers for the  $\pi$  vibrational states: a simple approximation of the potential energy about the equilibrium position up to quartic terms yielded an entirely unphysical description of the anharmonic couplings between separate  $\pi$  vibrational modes. We thus expect that the present theoretical results constitute a strong confirmation of our experimental assignment of the observed spectral lines to  $l-C_5H$  in its isotopic variants.

The short chain containing only five carbon atoms turns out to possess a very complicated dynamical internal structure. A detailed survey of available theoretical and experimental results on geometric, electronic, vibrational, and spectroscopic properties of linear carbon chains presented by us in [Ref.6] shows that also infinitely long chain of carbon atoms also possesses a collection of interesting phenomena. The experimental investigations mainly concern various properties (optical energy gap, vibrational frequencies, and spectroscopic properties in various environments) of finite chains containing up to a few dozens of carbon atoms. The theoretical efforts are focused on two main issues: 1) reconstructing and interpretation of the experimental results for short, finite-length chains and 2) constructing theoretical models capable of modeling physical properties of infinite chains. The presented survey is supplemented with extensive quantum calculations on the geometric, electronic, vibrational, and spectroscopic properties of finite and infinite chains. Two explicit models of the chains are considered: cumulenic with equidistant bond pattern and polyynic with alternated bond pattern. The models are studied using the SCC-DFTB method. The calculations for the infinite cumulene and polyne chains are based on standard solid state physics techniques, while the calculations for the finite chains use molecular orbital (MO) based quantum chemical methods. The correspondence between both theoretical descriptions is established. The presented results show that the physical properties (equilibrium geometry, electronic and vibrational densities of states, and the IR and Raman spectra) of relatively short ( $n > 100$ )

finite-length polyynes and cumulene chains ( $C_nH_2$  and  $C_nH_4$ , respectively)

Another very important group of carbon nanostructures consists of carbon fullerenes. Systematic analysis of such properties of various isomers can provide a theoretical basis for their looming experimental identification. The data for all isomers of  $C_{38}$ ,  $C_{40}$ , and  $C_{42}$  fullerenes presented in [Ref.5] is a part of a substantially larger research effort to characterize molecular structure and vibrational spectroscopic properties of pentagon/hexagon bearing carbon fullerenes  $C_{20}$ — $C_{180}$ . The results for the isomers of the fullerenes  $C_{20}$ — $C_{36}$  were presented previously. We report here the following properties of  $C_{38}$ ,  $C_{40}$ , and  $C_{42}$ : distribution of the CC distances, distribution of the valence CCC angles, density of electronic states, density of vibrational states, and the vibrational IR and Raman spectra. The properties of the eight most stable isomers of each fullerene are presented and discussed within the body of this article. The analogous properties of the remaining possible isomers of  $C_{38}$  (9 isomers),  $C_{40}$  (32 isomers), and  $C_{42}$  (37 isomers) are presented in Supporting Information accompanying this study. We define the stability of isomers via their HOMO-LUMO energy gap. This choice is motivated by the unusually high HOMOLUMO gap of the two most stable carbon fullerenes— $C_{60}$  and  $C_{70}$ —when compared with other small fullerenes. We believe that such an approach is more appropriate than to base an estimate of isomer abundance on relative stabilities regarding total energies, which do not necessarily correlate with the reactivity of a particular isomer. After all, the fullerene cages here in question are all high energy species, so much so that the penalty estimate for pentagon adjacency of about 18–25 kcal/mol is of no particular importance.

The  $C_{38}$ ,  $C_{40}$ , and  $C_{42}$  fullerene cages are small and contain high pentagon/hexagon ratios, necessarily including adjacent pentagon pairs. Some cages are not very spherical, either. It is rather unlikely that many of the structures analyzed in this study can be experimentally isolated in macroscopic quantities. There are two important aspects of the presented results: (i) computational assistance to experimental differentiation between possible structural isomers, (ii) theoretical study of the influence of topological structure of fullerenes on their electronic structures and vibrational spectroscopic properties. The latter aspect requires some discussion. It is clear that locally all the fullerenes have very similar structures: each carbon atom has three closest neighbors connected by single  $\sigma$  bond and a delocalized  $\pi$  bond. All of these neighboring carbon atoms are located in a similar distance. This situation extends also to the second-

closest neighbors: their number (6) is constant and the separation to them is also very similar. The local curvature in the vicinity of every atom is not very different (excluding very strained structures). These observations suggest that the physical and spectroscopic properties of these molecules can be possibly divided into two classes: those that depend only on the local structure and those that depend on the global topological structure. The difference between these classes should be easily observable in theoretical results and should provide experimentalists with specific molecular properties that can be used to discriminate between these similar isomeric structures. Various isomers of fullerenes described by identical chemical formula differ usually by the point-group symmetry. For structures possessing identical symmetry, the most convenient way to distinguish between them is using the Fowler-Manolopoulos index of every considered structure. The computed electronic densities of states may be useful to assist in the assignment of UV/VIS spectra, whereas vibrational spectroscopic data is directly comparable with the measured quantities. Together, the presented data should provide a valuable tool for the identification of small-cage fullerenes  $C_{38}$ ,  $C_{40}$ , and  $C_{42}$  synthesized even in small quantities.

The aforementioned projects determine the main direction of the scientific investigation in our research group. In addition to these projects a number of other related investigations is taking place that are closer or looser connected to the main investigation topic. Below, a short description of these projects is presented.

### **A. Intruder states in multireference perturbation theory: ground state of manganese dimer [Ref.4]**

A detailed analysis of a severe intruder state problem in the multistate multireference perturbation theory (MS-MRPT) calculations on the ground state of manganese dimer is presented. An enormous number of detected intruder states (>5000) do not permit finding even an approximate shape of the  $X^1\Sigma_g^+$  potential energy curve. The intruder states are explicitly demonstrated to originate from quasidegeneracies in the zeroth-order Hamiltonian spectrum. The electronic configurations responsible for appearance of the quasidegeneracies are identified as single and double excitations from the active orbitals to the external orbitals. It is shown that the quasidegeneracy problem can be completely eliminated using shift techniques despite of its severity. The resultant

curves are smooth and continuous. Unfortunately, strong dependence of the spectroscopic parameters of the  $X^1\Sigma_g^+$  state on the shift parameter is observed. This finding rises serious controversies regarding validity of employing shift techniques for solving the intruder state problem in multistate multireference perturbation theory. Various alternative approaches of removing intruder states (e.g., modification of the basis set or changing the active space) are tested. None of these conventional techniques is able to fully avoid the quasidegeneracies. We believe that the MS-MRPT calculations on the three lowest  $A_g$  states of manganese dimer constitute a perfect benchmark case for studying the behavior of MRPT in extreme situations.

## **B. Theoretical Investigation of Molecular Properties of the First Excited State of the Thiophenoxyl Radical [Ref.1]**

Accurate *ab initio* study of the lowest excited state ( $A^2B_2$ ) of thiophenoxyl radical is presented. The calculated equilibrium geometries, excitation energies, and harmonic vibrational frequencies show that the  $A^2B_2 \leftarrow X^2B_1$  excitation in  $C_6H_5S$  has different characteristic than the analogous transition in phenoxyl radical. Vertical excitation energies for other low-lying (<4.5 eV) excited states of thiophenoxyl radical are also presented and compared with available experimental data.

## **C. Rovibronic Bands for the Transition to the First Excited State of Phenoxyl Radical [Ref.2]**

Several rovibronic bands of  $C_6H_5O$  and  $C_6D_5O$  in their  $A^2B_2 \leftarrow X^2B_1$  transitions is observed in cavity ring-down experiment despite of their electronically forbidden character. A comparison of rovibronic contours and a consideration of vibrational wavenumbers of the upper state based on quantum-chemical calculations are able to provide vibronic assignments of observed bands and derive several experimental vibrational wavenumbers. Observed isotopic ratios of vibrational wavenumbers for the A state of  $C_6H_5O$  to those of  $C_6D_5O$  are in good agreement with the predictions from quantum-chemical calculations at the B3LYP/aug-cc-pVTZ level.

## **D. Theoretical study of noble-gas containing metal halides [Ref.3]**



Geometrical structures and energetic stability of noble-gas containing metal halides,  $MNgX$  and  $NgMX$ , ( $Ng = Ar, Kr, Xe$ ;  $M = Cu, Ag, Kr$ ;  $X = F, Cl, Br$ ) have been studied computationally using coupled cluster and perturbation theories. Two possible dissociation channels, (1)  $M + Ng + X$ , and (2)  $MX + Ng$ , and a reorganization reaction  $MNgX \rightarrow NgMX$  have been explicitly considered. The results suggest that the argon-containing compounds are unstable or very weakly bound. For most of the krypton- and xenon-containing species, well-defined  $M^{\delta+}NgX^{\delta-}$  and  $NgM^{\delta+}X^{\delta-}$  equilibrium structures have been found. Large reorganization barriers for some of the  $MNgX$  molecules, e.g.  $AuXeF$  and  $AuXeCl$ , indicate their considerable thermodynamic stability. We believe that direct observation of the most stable of the  $MNgX$  molecules might be possible in experiment.

## E. Parameterization of the SCC-DFTB repulsive potentials [Ref.8]

In this work, we derive and test a new automatized strategy to construct repulsive potentials for the self-consistent-charge density-functional tight-binding (SCC-DFTB) method. This approach allows to explore the parameter space in a systematic fashion in order to find optimal solutions. We find that due to the limited flexibility of the SCC-DFTB electronic part not all properties can be optimized simultaneously. For example, the optimization of heats of formation is in conflict with the optimization of vibrational frequencies. Therefore, a special parametrization for vibrational frequencies is derived. It is shown, that the performance of SCC-DFTB can be significantly improved using a more elaborate fitting strategy. A new fit for C and H is presented, which results in average error of 2.6 kcal/mole for heats of formations for a large set of hydrocarbons indicating that the performance of SCC-DFTB can be systematically improved also for other elements.

## Publications:

1. C.W. Cheng, Y.P. Lee, and H. A. Witek, "Theoretical investigation of molecular properties of the first excited state of thiophenoxyl radical", *J. Phys. Chem. A* **112**, 11998 (2008).
2. C.W. Cheng, H. A. Witek, and Y.P. Lee, "Rovibronic bands of the  $A^2B_2 \leftarrow X^2B_1$  transition of  $C_6H_5O$  and  $C_6D_5O$  detected with cavity ringdown absorption near  $1.2 \mu m$ ", *J. Chem. Phys.* **129**, 154307 (2008).
3. C.H. Mou and H.A. Witek, "Theoretical study of noble-gas containing metal halides", *J. Chem. Phys.* **129**, 244310 (2008)

4. C. Camacho, S. Yamamoto, and H. A. Witek, "Intruder states in multireference perturbation theory: ground state of  $Mn_2$ ", *J. Comput. Chem.* **30**, 468-478 (2009)
5. E. Małolepsza, Y. P. Lee, H. A. Witek, S. Irle, C. F. Lin, and H. M. Hsieh, "Comparison of geometric, electronic, and vibrational properties for all pentagon/hexagon-bearing isomers of fullerenes  $C_{38}$ ,  $C_{40}$ , and  $C_{42}$ ", *Int. J. Quantum Chem.*, **109**, 1999 (2009)
6. C.P. Chou, W.F. Li, H.A. Witek, and M. Andrzejak, "Vibrational Spectroscopy of Linear Carbon Chains", in "Spectroscopy, Dynamics and Molecular Theory of Carbon Plasmas and Vapors", edited by L. Nemes and S. Irle, World Scientific, 2009, Singapore
7. Y.J. Wu, H.F. Chen, C. Camacho, H. A. Witek, S.C. Hsu, M.Y. Lin, S.L. Chou, J.F. Ogilvie, and B.M. Cheng, "Formation and identification of interstellar molecule linear  $C_5H$  from photolysis of methane dispersed in solid neon", *Astrophys. J.*, accepted
8. M. Gaus, C.P. Chou, H.A. Witek, and M. Elstner, "Automatized parametrization of SCC-DFTB repulsive potentials: Application to hydrocarbons", submitted to *J. Phys. Chem. A*
9. W.F. Li, M. Andrzejak, and H.A. Witek, "Evolution of molecular properties. I. Geometric and electronic structure of conjugated systems.", submitted to *J. Phys. Chem. B*