

Final report for the project NSC96-2113-M-009-022-MY3

(Theoretical Modeling of Carbon Nanostructures)

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Introduction

In the present report, we discuss our accomplishments in modeling various physical and chemical properties of carbon nanostructures. These structures are a very popular topic in modern research world. The popularity of this field dates back to 90's and is closely connected to the discovery of the structure of the fullerene C_{60} . The development in this field, mainly in experiment but strongly guided by theoretical modeling, went in quite incredible direction, leading to a discovery of carbon nanotubes, nanoribbons, nanohorns, graphene flakes, etc. The best measure of the popularity of this research topic is the 2010 Nobel Prize in physics given to Andre Geim and Konstantin Novoselov for their ground-breaking work leading to methods of fabrication and characterization of the two-dimensional carbon crystal, graphene. Most of the effort toward synthesis and characterization of the carbon nanostructures naturally involves experimental techniques, but it should be highlighted that in many cases an invaluable insight originated from theoretical modeling, even in some cases the theoretical models or methods were in reality too crude to account for a given effect. We hope that our results will also assist experimental groups to predict and possibly synthesize new carbon nanostructures. We also hope that the results will give deeper understand of various phenomena occurring in such extended structures.

In this research report, we list the particular investigations we have been able to perform during the last 3 years. Some of them were accomplished and the final results have been already published. For many of them, however, the work is still in various stages of completeness, including fully finished projects awaiting writing up the associated manuscripts and still on-going projects in all possible level of advancement. Some of the scientific projects realized during the last 3 years in our group are not directly related to the topic of the present research grant, either resulting from the

previous grant (“Relativistic parametrization of the SCC-DFTB method”, NSC96-2113-M-009-015, -016) or originating with *a priori* unpredictable requests from experimental groups within the Department of Applied Chemistry and the Institute of Molecular Science, NCTU. These projects, often resulting in scientific publications, are also shortly discussed in this research report. The report is finalized with the list of publications resulting from the abovementioned investigations.

Main discoveries and conclusions

Our work on chemical and physical properties of carbon nanostructures mainly concerned various quantities that can be accessed using quantum chemical methods. Therefore, our investigations are focused on such properties as: energetics of various carbon structures and their aggregates, equilibrium and transition geometrical structures of carbon nanostructures, dipole and quadrupole moments, polarizability, harmonic vibrational frequencies, and vibrational IR and Raman spectra. The theoretical tool used for our analysis is the self-consistent-charge density-functional tight-binding (SCC-DFTB) approximation, which can be considered as a simplified version of density functional theory (DFT).

One of the most important research results concerns the behavior of Raman spectra of nanocrystalline diamonds (ND) while their size and shape is varied. The size evolution of the Raman spectra of octahedral and tetrahedral NDs with a diameter range of 0.3–2.9 nm has been studied using the DFT and DFTB methods. To the best of our knowledge, this is the first time that the size evolution of Raman spectra for molecules up to about one thousand atoms was followed using a quantum chemical method of similar accuracy to DFT. A clear and smooth convergence toward the Raman spectrum of a diamond crystal has been observed, particularly in the octahedral regime. The Raman spectrum of the largest studied octahedral structure, O8 ($C_{969}H_{324}$), is dominated by a single T_2 band at 1200 cm^{-1} corresponding to the optical phonons of diamond at Γ , and a comb of low-frequency bands located between 120 and 170 cm^{-1} , which correspond to the diamond’s acoustic phonons. In the tetrahedral regime, two additional spectral features are detected, at 1050 and 1450 cm^{-1} , which we assume will fade away for model systems larger than those studied here since they originate from surface effects. This assumption is based on

the fact that these features do not persist in the octahedral regime indicates, and therefore are expected to similarly fade away since the Raman spectra for both polyhedra types have to converge in the bulk limit. The position of the T_2 band for both families of structures is gradually blue-shifted with the growing size of the model. This suggests that one of the reasons for the observed discrepancy between the positions of the simulated ($\sim 1200\text{ cm}^{-1}$) and experimental ($1325\text{ to }1332\text{ cm}^{-1}$) band—in addition to that of the harmonic approximation and the inherently approximate nature of DFTB—may be the insufficiently large size of the models studied here. This observation particularly applies to the family of tetrahedral structures, for which the convergent trend in the evolution of the non-low-frequency bands requires large model systems.

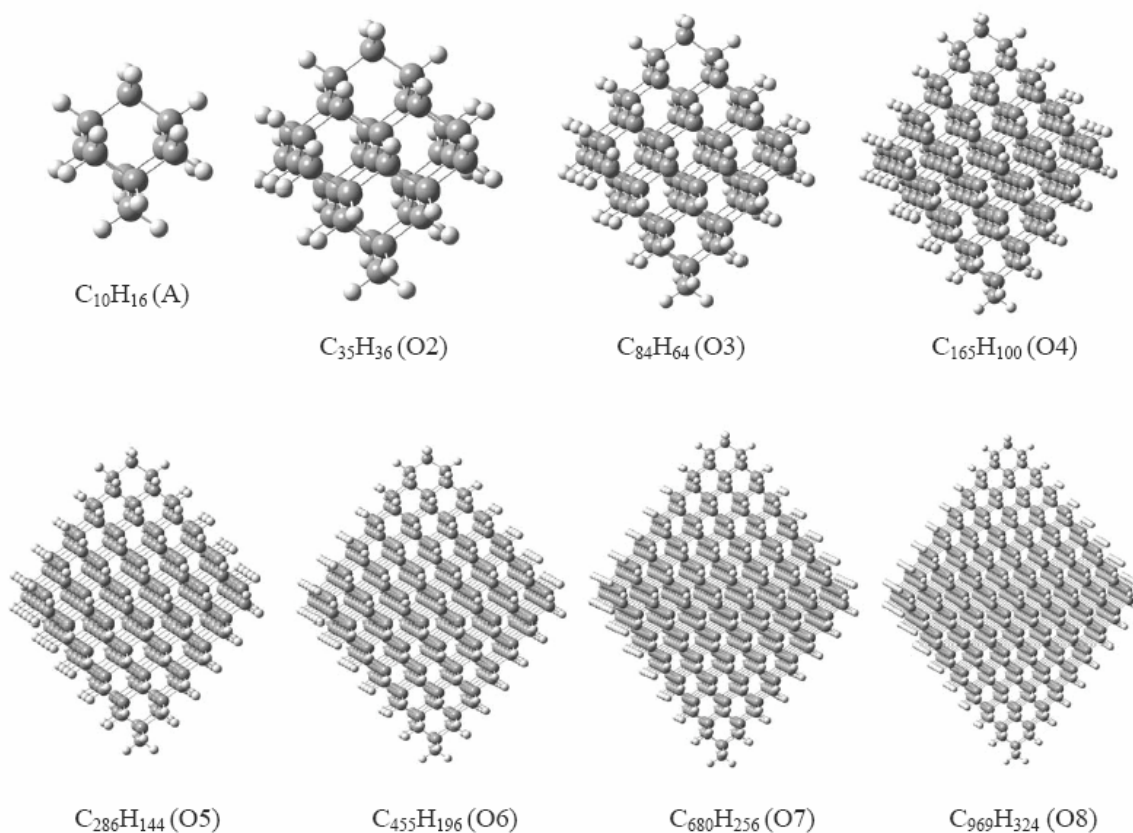


Fig. 1. Octahedral models of nanodiamonds used in our study of evolution of Raman spectra with varying size of the model. The model O8 with more than 1300 atoms is probably the largest molecule, for which Raman spectrum was ever modeled using quantum chemical method.

We obtained three important findings from this work. (i) We have given a quantitative relationship between the ND size and the position of the low-frequency Raman active peaks (equations 2 and 3) as a an analogue of the dependence of the frequency of the radial breathing mode (RBM) on the inverse diameter in single-walled carbon nanotubes. (ii) The Raman spectra evolution pattern depends quite strongly on the shape (here octahedral versus tetrahedral family) of the crystalline ND grains. To the best of our knowledge, the influence of the shape on the appearance of the ND Raman spectra has not been considered before. (iii) No evidence of other spectral features previously suggested for Raman characterization of ND samples is found in our simulations, in good agreement with previous considerations from experiments. Our work confirms the theoretical predictions made by Filik *et al.* that the only Raman activity expected for NDs is associated with the zone-center mode around 1325 cm^{-1} and the low-frequency cage-deformation and breathing modes. Studies of the effect of defects, different and irregular shapes, and surface functional groups on ND vibrational spectra are currently ongoing in our labs.

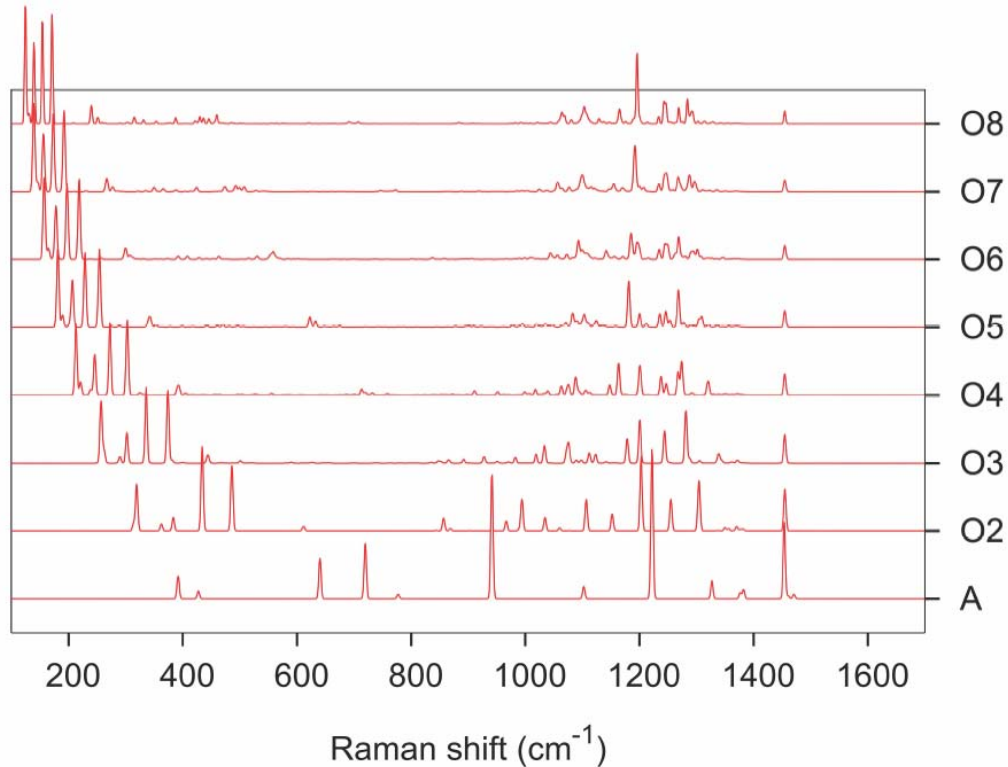


Fig. 2. Evolution of Raman spectra of octahedral nanodiamonds with growing size of the model.

Another very important finding obtained from our investigation concerns dramatically reduced IR signal for species encapsulated inside carbon nanotubes. Carbon nanotubes (CNTs) are highly polarizable due to their delocalized π -electrons and therefore molecules encapsulated in their inner spaces experience Faraday shielding, *i.e.* reduction of external electromagnetic fields. Moreover, electric moments of encapsulated molecules are screened due to induced mirror charges on the sidewalls of nanotubes. The two effects result in reduction of spectroscopic cross-sections for encapsulated molecules. We present experimental and theoretical evidence for significantly reduced infrared (IR) vibrational intensities of molecules upon adsorption inside single wall CNTs (SWCNTs). In the course of combined temperature programmed desorption and IR studies it was found that IR-intensities of molecules adsorbed endohedrally inside (endo) SWCNTs are reduced by a factor of ~ 30 relative to IR intensities of molecules adsorbed exohedrally (exo). Confirming this dramatic reduction are computed IR intensities for vibrations of acetone adsorbed on model systems of small (s)- and large (l)-diameter SWCNTs with C-O bond oriented parallel (\parallel) or perpendicular (\perp) to the sidewall predict reductions, which predict IR intensity screening in the order $\text{endo}(s) > \text{endo}(l) \approx \text{exo}\parallel(l) > \text{exo}\parallel(s) > \text{gas phase} \geq \text{exo}\perp$. The results raise questions on the applicability of IR vibrational spectroscopy for estimating the effectiveness of encapsulation processes, for the characterization of encapsulated molecules, and for the investigation of molecular level modifications that might occur inside CNTs. "Stealthy" molecular transport through CNT channels nearly undetectable to spectroscopic methods can be envisioned.

Another project concerned the investigation of the evolution of various physical properties of π -conjugated oligomers with the increasing length of the system. 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 π -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.

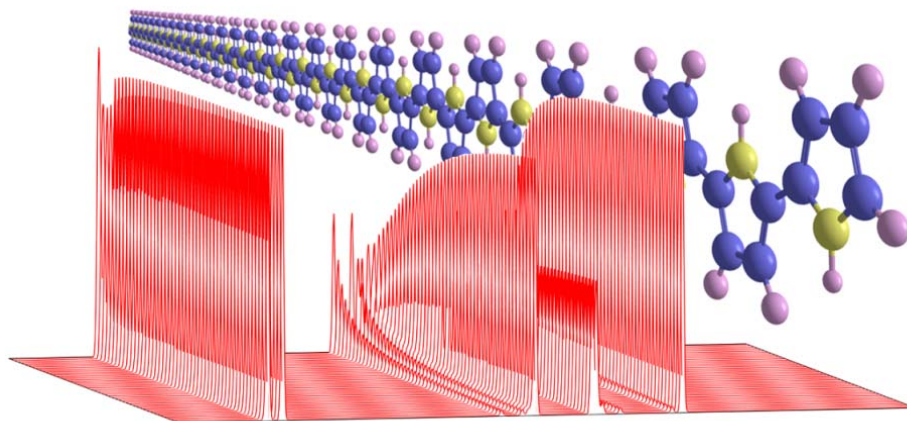


Fig. 3. Size-dependent distribution of the bonds inside finite-length pyrrole oligomers varies with the length of the chain. The convergence is observed for surprisingly short chains.

We are fully aware that the results obtained within the framework of the SCC-DFTB 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 π -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 π -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, we have studied 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 σ^+ 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 $^{13}\text{C}_5\text{H}$, which correspond directly to the species observed in our experiments. The mean absolute deviation between the corresponding computed and measured fundamental σ^+ 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 π 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 π 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 polyene 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 polyene 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

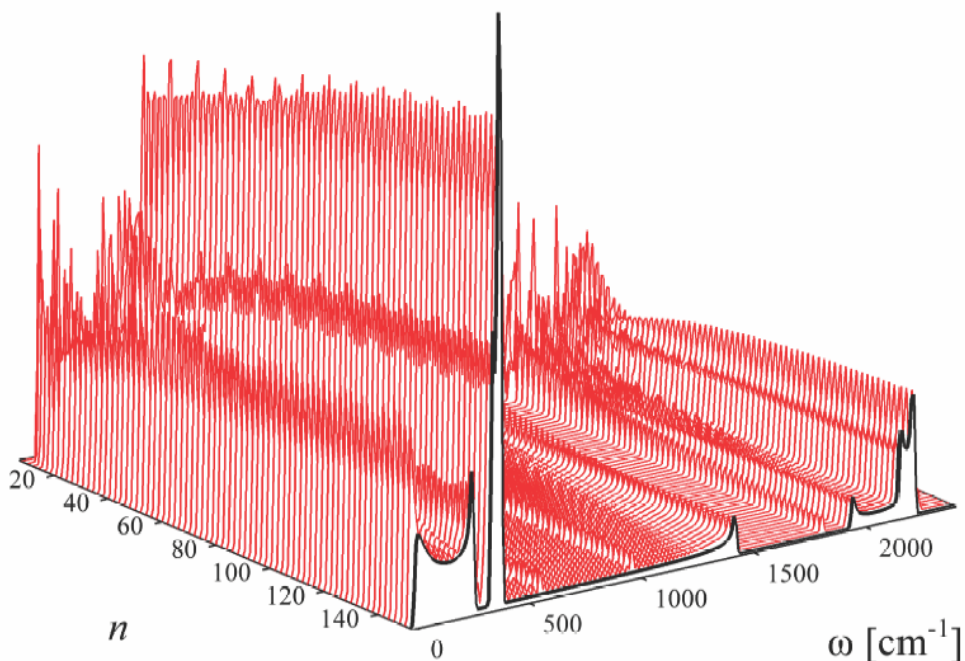


Fig. 4. Vibrational density of states plotted as a function of the size of finite-length polyyn chain. The limiting black curve corresponds to the solid-state calculations.

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 σ bond and a delocalized π bond. All of these neighboring carbon atoms are located in a

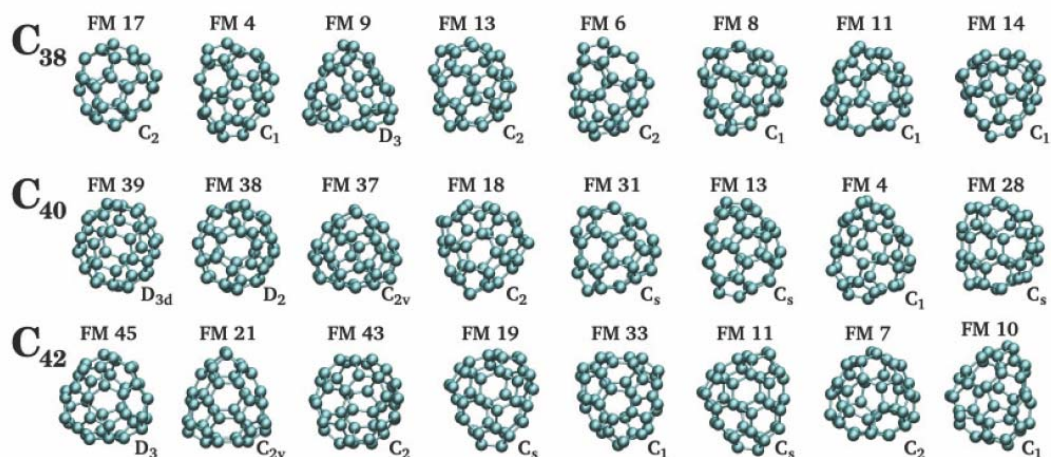


Fig. 5. The most energetically stable isomers of fullerenes C_{38} , C_{40} , and C_{42} . These models were used to compare various physical and chemical properties of these systems in our study.

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.

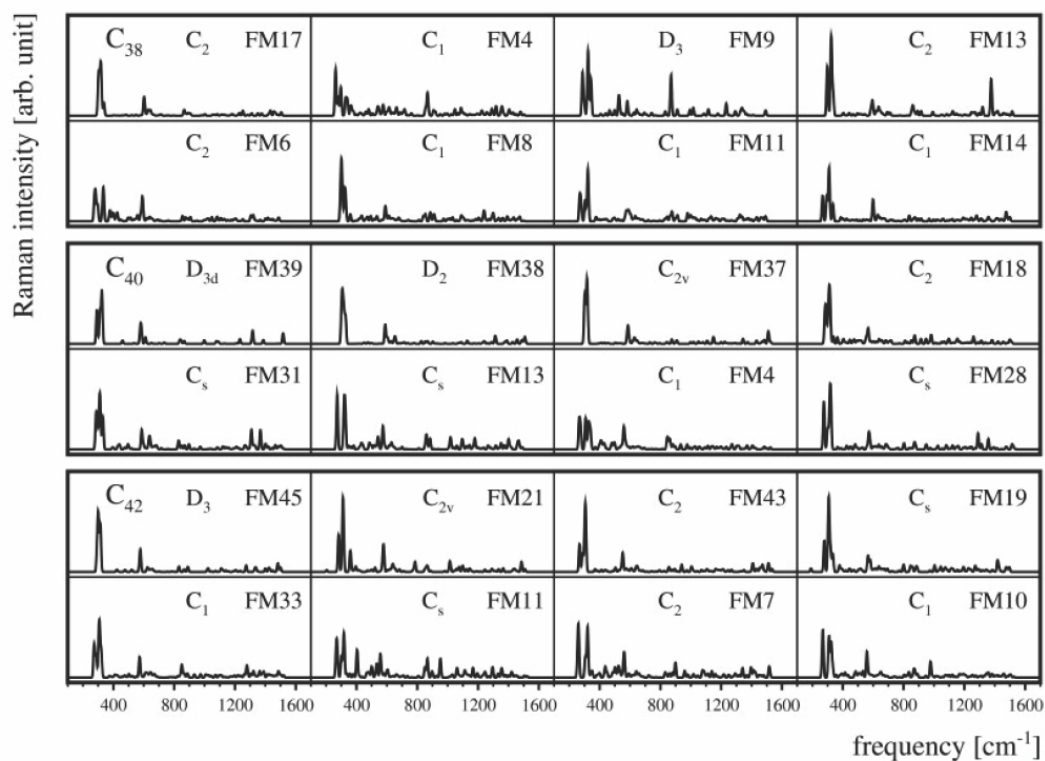


Fig. 6. Raman vibrational spectra of the most stable isomers of fullerenes C_{38} , C_{40} , and C_{42} . Note close resemblance of the general structure of the spectra and simultaneous small but very distinct differences between the particular features.

Additional research

In this Section we discuss various projects not directly related to the main topic of the current research grant. The work on these projects was motivated by collaborations within the Department of Applied Chemistry, NCTU. In some cases, it is a continuation of previously pursued research projects, especially those funded by the previous NSC96-2113-M-009-015, -016 grant “Relativistic parametrization of the SCC-DFTB method”.

A. Intruder states in multireference perturbation theory: ground state of manganese dimer

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 raises 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

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

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

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

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.

F. Barrierless reactions between two closed-shell molecules. I. Dynamics of $F_2+CH_3SCH_3$ reaction

A detailed experimental and theoretical investigation of the first-reported barrierless reaction between two closed-shell molecules [J. Chem. Phys. 127, 101101 (2007)] is presented. The translational energy and angular distributions of two product channels, $HF+CH_2SFCH_3$ and $F+CH_3SFCH_3$, determined at several collision energies, have been analyzed to reveal the dynamics of the studied reaction. Detailed analysis of the experimental and computational results supports the proposed reaction mechanism involving a short-lived $F-F-S(CH_3)_2$ intermediate, which can be formed without any activation energy. Other possible reaction mechanisms have been discriminated. The decay of the intermediate and competition between the two product channels have been discussed.

G. Theoretical Investigation of Molecular Properties of the First Excited State of the Phenoxy Radical

A theoretical study of molecular, electronic, and vibrational properties of the first excited state of the phenoxy radical, A^2B_2 , is presented. The calculated molecular geometries, vertical and adiabatic excitation energies, and harmonic vibrational frequencies are compared with analogous results obtained for the ground state. The calculated excitation energies correspond well to experimental data. The harmonic vibrational frequencies of the A^2B_2 and the ground state are similar except for modes involving the vibrations of the CO bond.

H. Choosing a proper complete active space in calculations for transition metal dimers: Ground state of Mn_2 revisited

The potential energy curve of the ground state of Mn_2 has been studied using a systematic sequence of complete active spaces. Deficiencies of the routinely used active space, built from atomic $4s$ and $3d$ orbitals, has been identified and discussed. It is shown that an additional σ_g orbital, originating from the atomic virtual $4p_z$ orbitals, is essential for a proper description of static correlation in the $^1\Sigma_g^+$ state of Mn_2 . The calculated spectroscopic parameters of the $^1\Sigma_g^+$ state agree well with available experimental data.

The calculated equilibrium bond lengths are located between 3.24 and 3.50 Å, the harmonic vibrational frequencies, between 44 and 72 cm⁻¹, and the dissociation energies, between 0.05 and 0.09 eV. An urgent need for an accurate gas-phase experimental study of spectroscopic constants of Mn₂ is highlighted.

I. Interpreting the experimental UV/vis spectrum of Cl + CS₂ complex

Accurate multireference configuration interaction and time-dependent density functional calculations have been performed to interpret the experimental UV-vis spectrum of the CS₂/Cl complex in the spectral region 320-550 nm. The molecular structure of the complex responsible for the previously observed UV-vis spectrum is recognized as ClSCS, not ClCS₂. Two low-lying excited states of ClSCS, responsible for its optical absorption, have been identified and analyzed. Optical excitation of ClSCS leads to the excitation-specific bond elongation that may lead to photofragmentation of the molecule. In addition, experimental conditions for verifying the presence of ClCS₂ are identified and detailed characterization of its optically active excited states with possible photofragmentation pathways is given.

J. Determination of the ground state of the scandium dimer

A systematic investigation of low-lying states of Sc₂ using multireference perturbation theory (NEVPT2 and NEVPT3) indicates that the ground state of this system is ⁵Σ_u⁻ with $r_e=2.611$ Å, $\omega_e=241.8$ cm⁻¹, and $D_e=1.78$ eV. An excellent agreement between the second- and third-order NEVPT results and between the computed and experimental values state suggests high accuracy of our predictions.

K. Demonstration that multireference perturbation theory with one-electron zeroth-order Hamiltonian cannot be used for studying transition metal clusters

Prediction of a false ground state with popular variants of multireference perturbation theory (CASPT2 and MRMP) is reported for a remarkably simple chemical system: the Sc₂ molecule.

Resulting publications

1. C.W. Cheng, Y.P. Lee, and H. A. Witek, "Theoretical investigation of molecular properties of the first excited state of phenoxy radical", *J. Phys. Chem. A* **112**, 2648 (2008)
2. Y.-J. Lu, L. Lee, J.-W. Pan, H. A. Witek, and J. J. Lin, "Barrierless reactions between two closed-shell molecules. I. Dynamics of $F_2 + CH_3SCH_3$ reaction", *J. Chem. Phys.* **128**, 104317 (2008)
3. C. Camacho, S. Yamamoto, and H. A. Witek, "Choosing a proper complete active space in calculations for transition metal dimers: Ground state of Mn_2 revisited", *Phys. Chem. Chem. Phys.* **10**, 5128 (2008).
4. C.W. Cheng, Y.P. Lee, and H. A. Witek, "Theoretical investigation of molecular properties of the first excited state of thiophenoxy radical", *J. Phys. Chem. A* **112**, 11998 (2008).
5. 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).
6. C.H. Mou and H.A. Witek, "Theoretical study of noble-gas containing metal halides", *J. Chem. Phys.* **129**, 244310 (2008)
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Post-doctoral fellow report

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I have spent nearly four months working in the Department of Applied Chemistry and Institute of Molecular Science at the National Chiao Tung University in Hsinchu, in the group of professor Henryk A. Witek.

I find this stay a very inspirational, and many subjects that came out in our discussions with professor Witek and his co-workers have kept me busy till now. The major topics of our work went along two lines: the properties of extended systems studied by means of more or less approximate methods (SCC-DFTB, DFT/TDDFT), and the multireference calculations for medium size molecules. The former topic concerned an investigation of various physical and chemical properties of oligomers built from heterocyclic aromatic compounds as a function of the lengths of the oligomer. Such systems can be treated as realistic models for infinite polymer chains, which never show the idealized infinitely long chain in experimental samples. Our results demonstrated that the properties of extended systems of this type converge relatively fast with the length of the chain, explaining in part the uniform characteristic of various polymers prepared in different conditions and characterized by substantially distinct effective chain lengths. The results obtained in this work are quite fascinating and currently we are preparing a manuscript covering main results of our investigations. The latter subject, a study of electronic spectra of bithiophene using a series of active spaces, has proved to be especially fascinating, and we have been able to perform successful CASSCF/CASPT2 calculations for a number of systems, for which the previous theoretical reports seemed controversial. The most thoroughly studied system is bithiophene, for which no unambiguous assignment exists even for its lowest absorption band. In two papers Rubio *et al* claimed, on the grounds of the multireference calculations, that a pair of quasi-degenerate excited states of B_u symmetry is responsible for the lowest absorption band of bithiophene. We have proved that these results were incorrect and proposed an improved assignment, consistent with chemical intuition, experimental findings and results of alternative quantum chemical methods. A series of papers containing the results of our work is about to be published, and a poster “*The elusive 1B_u states of Bithiophene –*

CASSCF/CASPT2 study” has been presented on two international conferences (Psi-k 2010, Berlin, Germany and International Symposium of Theoretical Chemistry, STC-2010, Muenster, Germany). The experience we have gained can be also used in our future co-operation, which we hope to continue to our mutual satisfaction.

Apart from the two main topics we have attempted a few subjects that show promise, even though work is still needed to obtain conclusive results. One of them is the rationalization of the supersonic jet fluorescence spectra of *o*-cyano-*p*-methylanilin, which show several low energy bands with non-Condon intensity distribution that have not yet been assigned. This work is in colaboration with Dr Przemyslaw Kolek from Jagiellonian University, who provided the experimental results and insight. The working hypothesis is that it is the torsional movement of the methyl group that is responsible for the bands in question. I have computed the potential for the methyl group rotation with respect to the benzene ring for the ground and the excited molecular state, in order to model the vibronic structures in 1D numerical procedure. The low symmetry of the system, however, and sizable couplings with other low-energy vibrations of the system hindered the work, as more complicated (multidimensional) model seems to be required. We intend to carry on the work in this field, having completed the multireference calculations mentioned above.

Besides the scientific aspect of my work in Hsinchu, I would like to stress the very comfortable conditions of stay that I have been offered. I was provided with accommodation in a very convenient distance to the laboratory, an unlimited computer time and invaluable technical assistance that helped me learn the software and computational environment I was to use. Professor Witek and his group showed a truly great hospitality, which I hope to return whenever our future cooperation brings the chance to welcome them in Krakow.