Small Silicon Clusters with 3d Transition Metal Atom Impurities.

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The electronic properties of silicon devices can be profoundly influenced by the presence of Transition Metal (TM) impurities or deposited TM films. Extensive experimental and theoretical efforts have been devoted to the behavior of TM impurities in a silicon host or on a silicon (Si) substrate. However, despite many years of basic research, the understanding of the formation and bonding mechanisms in TM – Si systems remains very poor. The present contribution is based on the realization that small TM – Si clusters provide a medium suitable to obtain detailed knowledge of the metal – silicon interactions which determine both the geometric and the electronic structure of TM – Si contacts.

In a series of preliminary computational studies, the geometries, stabilities and bonding related features of CuSi\(_N\) (\(N = 2, 4, 6,...,12\)) were explored /1-3/ on the basis of a DFT/B3LYP approach. We continue these studies by investigations on TMSi\(_N\) where TM = Sc, Ti, V, Cr, Mn, Fe, Co, Ni and \(N = 4, 6\). The most pronounced difference between this series of TM impurities and the previously investigated Cu atom consists in the much stronger participation of the 3d shell of the TM species in the interaction between the metal atom and its Si environment than found in the case of Cu. Correspondingly, high spin states have to be analyzed for each of the systems considered. The impact of spin orbit coupling on the ground state energies of the investigated clusters is discussed.

As in the preceding work on CuSi\(_N\), we classify the resulting cluster geometries into substitutional, adsorption and center sites. Special emphasis will be placed on the unit TMSi\(_6\); the respective results will be compared with the findings on both CuSi\(_6\) and NaSi\(_6\) /4/ which have been studied extensively. As much as these latter species, the former ones are shown to stabilize preferentially in substitutional geometries derived from the Si\(_7\) cluster as structural model. Both CuSi\(_6\) and NaSi\(_6\), however, behave as electron donors, while a reversal of this direction of charge transfer appears to be characteristic of TMSi\(_6\).

References

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Ab initio Studies of Silicon Alpha Effect on the Intramolecular Ring-Opening Reactions of Epoxysilanes

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Intramolecular Nucleophilic substitution reactions are controlled by many factors:- transition state energy, proximity of the reacting functional groups, and the size, energy & stability of the ring product. For the cyclization of -aminoalkyl bromides, the reaction of 1-Amino-4-bromobutane, which gave a five-membered ring was more reactive than the reaction of 1-Amino-5-bromopentane which gave a six-membered ring. In order to investigate the influence of an \textsuperscript{a}-Silyl group in the energetics of these intramolecular nucleophilic substitution reactions, we conducted the ab-Initio studies of compounds 1-4 below. The results showed that the trimethylsilyl group had an overriding influence over the controlling factors stated above in controlling the cyclization reactions of the systems studied.

[Diagram of compounds 4 and 5]

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Influence of Trimethylsilyl and Phenyl Groups on the Deprotonation of Organosilicon Compounds I & II

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Many functionalized organosilicon compounds have been deprotonated alpha to silicon with some selected bases and under certain conditions. α, β-Epoxysilanes are synthetically useful because they can be converted into carbonyl compounds where the carbonyl group is regiospecifically placed at the alpha or beta carbon of the original epoxide. Since many organosilicon compounds can serve a carbanion equivalent, we decided to study compounds I & II to examine the variation of trimethylsilyl and phenyl groups in stabilizing their alpha beta anions. In compound I, deprotonation at the alpha position predominated and has a lower barrier. However, in compound II, the deprotonation at the beta position was favored.

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Ultrasonic and Thermodynamic Studies of Glycine in Aqueous Electrolytic Solutions

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Densities, d, and ultrasonic speed, u of glycine in aqueous NaCl and MgCl₂ solution were measured at different molarities at 308K. From these experimental data, adiabatic compressibility, Kₛ, apparent molar compressibility, φΚₛ, apparent molar volume, φᵥ, and molar sound velocity, Rₘ, hydration number Hₙ, acoustic impedance, Z, partial molar volume, φ₀ᵥ, and partial molar compressibility, φ₀Κₛ, were calculated for all the ternary systems. The data have been interpreted in terms of solute-cosolute and solute-solvent interactions. These results show that dipole-dipole interaction and ion-solvent interaction are strong in case of glycine aqueous NaCl and MgCl₂ solutions.
A Theoretical Study of Structure and Properties of Uric Acid: A Potent Antioxidant

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Uric acid, a purine metabolic end product in human is a white odorless tasteless crystalline molecule. It has a weak acidic character and is barely soluble in water and insoluble in alcohol and ether. It is present in human blood in appreciably high concentration and acts in the human defense system as an antioxidant by protecting living organisms against oxidative and free radical damage. Specifically, urate—the salt form of uric acid acts as a singlet oxygen, OH radical, and oxo-heme scavenger. This protective role of uric acid has, therefore, been cited as an important factor in the prevention of aging and cancer. However, high concentration of uric acid in human causes the deposition of crystals of sodium urate in joints which leads to disease called gout.

A detailed study of tautomeric properties of uric acid and its different anions were performed at the Density Functional Theory level employing B3LYP functional. Initially, the relative stability of different possible neutral tautomers were determined using 3-21G(d,p) basis set and this was followed by computation with 6-31G(d,p) basis set for selected stable tautomers. For different possible anions the 6-31++G(d,p) basis set was used. The effect of aqueous solvation on the relative stability of neutral and anionic species was considered using polarized continuum model. The keto form of the molecule is found to be most stable in the gas phase and in aqueous medium. Among monoanions, the anion obtained by deprotonation of the N3 site is most stable, while among dianions, the anion obtained by deprotonation of N3 and N7 sites both is the most stable both in the gas phase and in aqueous medium. Different properties of neutral and anionic form of the uric acid in the gas phase and in aqueous media are discussed.
Theoretical Study of Vinyl-Vinyl Coupling on Platinum Group Metals

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Vinyl-vinyl coupling is a well-known reaction for conjugated dienes synthesis widely used under catalytic conditions. Most modern practical applications are realized based on palladium complexes as catalysts [1], in addition, platinum (IV) examples have been also reported [2].

Recently we have performed B3LYP density functional study of catalytic acetylene conversion reaction [3], which involves triple bond activation via external nucleophile addition step leading to mono- and bis-\(\sigma\)-vinyl derivatives (2 and 3 on Scheme 1) followed by vinyl-vinyl coupling as product releasing step. Detailed investigation of \(\text{C}_\text{SP2}-\text{C}_\text{SP2}\) reductive elimination revealed several peculiarities [4] compared to the processes involving \(\text{C}_\text{SP3}\) atoms of alkyl groups.

Particularly, it were found that C-C bond formation may be performed via two pathways corresponding to \(s\)-trans and \(s\)-cis conformations of buta-1,3-diene unit in the transition states. Asymmetric nature of vinyl-vinyl coupling allows the reaction to proceed via three different transition states (two enantiomers and a meso form).

A theoretical density functional study of the vinyl-vinyl coupling reaction has been performed for a wide range of platinum group metal complexes and suggested the similar C-C reductive elimination mechanism (Scheme 2).
Metal and ligand dependence study (M=Pd, Pt, Rh, Ir, Ru, Os; L=NH$_3$, PH$_3$, Cl, Br, I) were undertaken to investigate electronic and steric effects as well as steric effects induced by substituents in the vinyl groups (E/E, E/Z and Z/Z stereoselectivity). Detailed information on energetics, structural properties, metal-carbon bond strength and effect of solvent will be presented and discussed together with available experimental data.

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**References**

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Correction of Near-Degeneracy Effects in 2nd Order Perturbation Theory

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Perturbation theory is a very valuable and efficient tool for theoretical chemistry. It is mainly used to estimate the electronic correlation energy of chemical systems but also to access weak interactions in various areas like intermolecular interactions for instance. Albeit some inconveniences (not variational, slow convergence of the series), perturbation theory limited to second order presents a large variety of advantages. It is somewhat simple, size-consistent, implemented in numerous quantum chemistry packages, invariant under unitary transformation, and its first and second derivatives are available analytically.

The energy correction, at second order is

\[ -\sum_k \frac{|V_{0k}|^2}{E_k - E_0} \]

which diverges in the near-degeneracy case, that is when \( E_k = E_0 \), where \( E_k \) is the zero order energy of state \( k \) and \( E_0 \) is the zero order energy of the ground state. \( V_{0k} \) is a matrix element of the perturbation.

Perturbation theory relies on two assumptions:
- matrix elements should be small, compared to the zero order term
- energy differences between the ground and excited states must be not too small.

We will focus our attention on the second point. When the ground state and one excited state are degenerate, standard perturbation theory accounted for it. However, in case where the energy difference is close to zero (near degeneracy), one needs to apply quite expensive multireference formalisms (MRCI\(^3\), MRCC\(^4\), MRPT\(^5\), CASPT\(^6\)) to obtain reliable numerical results. Other solutions exist, cheaper with respect to computer facilities, like QDPT\(^7\) which faces major dilemmas, or damping parameter methods\(^8\) where the damping factor is not determined in a straightforward manner.

In this paper we present the Degeneracy Corrected Perturbation Theory to second order (DCPT2)\(^9\). This method, based on single determinant reference function (therefore less computer time consuming than multireference formalism\(^3-6\)), does not need any \textit{a priori} determined factor. It can be considered as an approximation of the Self-Consistent evaluation of 2nd order correlation energies of Lepetit and Malrieu (SCPT2)\(^10\).

The poster contains an overview of DCPT2 and its properties. We compare our results with those obtained with the QDPT2 method of Szabados and Surjan\(^8\) and with SCPT2\(^10\), for simple chemical systems using both the Møller-Plesset\(^11\) and the Epstein-Nesbet\(^12\) partitioning. Finally, we conclude about the strength and weakness of the present status of our method, and about its future applications and developments.
References

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The Unique Spectroscopic Behaviour of the Fe(III)-nitroprusside: A DFT Study on the Metastable States Including the Vibronic Coupling in the Ground and in the Lowest Excited States

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Upon irradiation with visible light in the region 350-600 nm the red coloured compound Na$_2$[Fe(CN)$_5$NO] with a nitrosyl Fe-NO bond in the ground state (GS) can be transformed with up to 50% yield into blue-red metastable excited electronic states (ES). /1-3/ At temperatures below 150 K the system can freeze out and reside in these states for a very long time, before converting reversibly back to the GS, either thermally (by heating above 150 K) or by excitation with a red light (800-1000 nm). The colour change associated with the generation of these ES has been proposed as a basis for reversible storage and reproduction of information using light at two different wavelengths. In order to rationalise the unique photophysical behaviour of this system we have performed calculations on the electronic and geometrical structure of the [Fe(CN)$_5$NO]$^-$ anion within the density functional theory (DFT) utilising the Amsterdam Density Functional (ADF) package. Geometry optimisations of the anion for the linear nitrosyl Fe-N-O, the iso-nitrosyl Fe-O-N ($C_{4v}$-symmetry) and the side-on bonded NO-ligand with a three centre Fe-N-O-bond ($C_s$ symmetry) and a critical evaluation of the total bonding energies of these structures as well as of those of the lowest ES with the same geometry or partly or totally geometrically relaxed configurations has lead to the following results:

The geometry with a linear Fe-N-O arrangement possesses the lowest energy in agreement with structural data representing the lowest minimum of adiabatic potential energy surface of the ground state (GS-APES). Calculated bond distances and bond angles compare nicely with reported structural data. /2/ The short Fe-N distance (1.66 Å) reflects a remarkably strong Fe-N bond. By using a full analysis of the vibrational modes of the complex anion we have identified two more local minima belonging to the GS-APES both of which are higher in energy than the GS minimum. The first one, denoted by MS2, contains side-on coordinated (bidentate) NO-group and is calculated 1.28 eV above the GS showing Fe-N and Fe-O bond lengths of 1.857 Å and 2.056 Å, respectively. The obtained geometrical parameters for this structure match perfectly with structural data from X-ray diffraction studies of irradiated samples. /2/ The second local minimum, denoted MS1, is found to be even higher in energy than MS2 (1.53 eV above the GS) and corresponds to a geometry with a linear Fe-O-N iso-nitrosyl linkage (calculated Fe-O distance 1.759 Å). We have been able to locate the two corresponding transition states (TS) on the GS-APES exhibiting relatives of 1.68 eV (TS1, connecting GS and MS2 and possessing a bent Fe-N-O moiety) and 3.08 eV (TS2, connecting MS2 and MS1 and possessing a bent Fe-O-N moiety). Remarkably, both TS energies are higher than the lowest excited triplet and singlet states when considering the underlying Fe-N-O and Fe-O-N angles for TS1 and TS2, respectively. Thus, in the vicinity of such angles, it is not TS1 and TS2 of the GS-APES which govern the energy barriers for thermal deactivation from MS2 to GS and from MS1 to MS2, but the lowest excited singlet and triplet states. Our new results compare well with data from differential scanning calorimetry (DSC), which predict three states with two of them very close in energy (1.0 and 1.1 eV above GS) but distinctly different from the third one (GS). /3/
Based on our calculations which give for MS2 and MS1 energies of 1.28 and 1.53 eV above the GS, we assign the metastable states at 1.0 eV and 1.1 eV to MS2 and MS1, and thus to the side-on bonded NO and to the Fe-O-N linkage isomers, respectively, in accordance with earlier results using periodic DFT type of calculations.\(^4\) In addition, we find the side-on bonded MS2 structure in the eclipsed conformation, i.e. the Fe-NO plane coincides with one \(\sigma_v\) plane of the \(C_{4v}\) structure, is energetically favoured by about 0.06 eV compared to a staggered conformation, where the Fe-(NO) plane coincides with one \(\sigma_d\) plane. Therefore, we propose a third metastable state that can be identified with the side-on bonded NO in the staggered conformation. We note that there is a reasonable agreement between calculated and experimental (from DSC) barriers for the thermal deactivation from MS2 to GS (exp. 0.5 eV, calc. 0.4 eV) and from MS1 to MS2 (exp. 0.7 eV, calc. 1.15 eV). Keeping in mind that two excited state potential surfaces cross the GS-APES in the region of the transitions states TS1 and TS2 (see above) and thus lead to a lowering of the energy barrier for thermal deactivation, the experimentally derived energy barriers are pretty well reproduced.

Using geometry optimisations on the lowest excited triplet and singlet states produced upon exciting one electron from the \(2b_2\) to the \(9e\) antibonding molecular orbitals we have been able to characterise these states as well. Jahn-Teller coupling in the ES that are due to the nitrosyl and iso-nitrosyl coordination leads to large shifts along the Jahn-Teller active distortion coordinate that corresponds to bending of the linear Fe-N-O (for GS) and Fe-O-N (for MS1) angles. Energy minima have been found at values of 141.4° (\(\delta\text{FeNO}\)) and 141.3° (\(\delta\text{FeON}\)), respectively. Being intermediates in their geometry between the linear Fe-N-O and Fe-O-N and the side-on bonded Fe(NO) structures these excited states provide an easy way for photoisomerisation of the linear GS (Fe-N-O) and MS1 (Fe-O-N) structures toward the side-on coordinated geometry of MS2 upon exciting with blue and red light, respectively.

We have also investigated the vibronic stabilisation energies when starting from the higher symmetric \((C_{4v})\) GS and MS1 structures. This allows for the first time to characterise excited state JT distortions in the doubly degenerate \(^1E\), \(^3E\) states for linear Fe-N-O and Fe-O-N bonds and, moreover, to correlate the evaluated vibronic parameters with the N-C-Fe(NO) bond changes accompanying the photoisomerisation process. The theoretical results have been applied to spectroscopic data from literature and our own measurements including highly resolved electronic absorption spectra that show rich vibronic fine structures at low temperatures, as well as infrared, Raman and resonance Raman spectra. In the light of these results a thorough discussion of the mechanism of photoisomerisation in the [Fe(CN)\(_5\)NO]\(^{2-}\) anion will be presented elsewhere.\(^5\)

References

5. M. Atanasov and T. Schönherr, to be submitted in the THEOCHEM issue of CCTCC.
The Stereochemical Lone Pair Activity of Main Group Molecules and Complexes - an Improvement of the Valence Shell Electron Pair Repulsion Model on the Basis of Density Functional and Vibronic Coupling Calculations

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The steric "lone pair" effect is a well-known phenomenon in chemistry. The "Valence Shell Electron Pair Repulsion Model" by Gillespie and Nyholm is used to rationalise the shapes of molecules and clusters in solids of main group elements possessing one or more lone pairs in the valence shell. We have studied the ground and the lowest excited states of such molecules in their highest possible parent symmetry and in the distorted geometry by means of density functional (DFT) calculations. The energies and geometries are obtained from geometry optimisations, whereby for the analysis of the displacement path connecting the two geometries a vibronic pseudo Jahn-Teller coupling model was applied. Explicitly we studied molecules AX\textsubscript{3} (A:N\textsuperscript{III}, P\textsuperscript{III}, As\textsuperscript{III}, Sb\textsuperscript{III}, Bi\textsuperscript{III}; X=F, Cl, Br, I and H) in D\textsubscript{3h} and C\textsubscript{3v} symmetry, asking for the driving force behind the geometric transition \textsuperscript{1}. We extended our investigations to the higher coordination numbers CN(=n; n=4-6): AX\textsubscript{n}(n-3)\textsuperscript{-} where the parent symmetries are expected to transform to the following lower-symmetry polyhedra by the vibronic coupling model: T\textsubscript{d} → C\textsubscript{2v} (n=4); D\textsubscript{3h} → C\textsubscript{2v}(C\textsubscript{4v}) (n=5) and O\textsubscript{h} → C\textsubscript{4v}, C\textsubscript{3v}, C\textsubscript{2v} \textsuperscript{2,3}. On the basis of these results, we have been able to develop criteria allowing to predict whether a distortion from the high symmetry structure actually occurs and to which extent. The fast availability of reliable results from DFT calculations provides a sound background for attacking this problem on a broader basis. It is shown that the driving force for distortions from higher to lower symmetry decreases according to the sequences

\[ X : F > Cl > Br > I \quad (A : N \text{ to } Bi) \; ; \quad A : N > P > As > Sb > Bi \quad (X : F) \]

the dependence on A being only small or not present for Cl to I. Furthermore this force strongly decreases with increasing CN. Interestingly enough it is the vibronic coupling strength, which is the energetically deciding quantity behind the lone pair activity. As we have shown \textsuperscript{1-3} the latter is directly connected with the chemical hardness: the hardest molecules are the most susceptible to vibronic coupling.

In this contribution we report about a further extension of our studies to the BX\textsubscript{4} molecules of the 6th period (B=S\textsuperscript{IV}, Se\textsuperscript{IV}, Te\textsuperscript{IV}, Po\textsuperscript{IV}; X=F, Cl, Br, I) \textsuperscript{4} and compare these results with those for AX\textsubscript{3} on one hand and with the also neutral AX\textsubscript{3} species on the other hand. Preliminary calculations show that the stereochemical activity of the lone pair increases in the sequences (2), i.e. again: the harder the ligand and B are, the more pronounced is the energy stabilisation of the distorted (C\textsubscript{2v}) structure with respect of the undistorted one (T\textsubscript{d}).

\[ F >> Cl \geq I, Br \; ; \quad S > Se, Te \]

(2)

In difference to the AX\textsubscript{3} molecules, which are all pyramidal (C\textsubscript{3v}) in the ground state energy minimum, the BX\textsubscript{4} molecules with B=S, Se, Te and X=F, Cl are the only ones, which are predicted to distort; the other species are characterised by a single energy minimum at T\textsubscript{d} geometry. However, compared to the corresponding closed shell ions (Si\textsuperscript{IV} - Si\textsuperscript{IV}, Ge\textsuperscript{IV} - Se\textsuperscript{IV}, Sn\textsuperscript{IV} -
Te$^{IV}$, the molecules with s$^2$-type lone pairs and a regular T$_d$ geometry possess potential surfaces which are rather flat along the displacement path of the (lowest energy) vibronically active $\tau_2$ mode. It is therefore expected that these molecules also display soft mode behaviour in the solid state. The physical background for cooperative phase transitions due to lone pair activities in such cases is discussed and an outlook for further theoretical studies and applications will be given.

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4. M. Atanasov, D. Reinen and T. Schönherr, to be submitted in the Theochem issue of the CCTCC.
Influence of Parameters in Repulsive Potentials of the Ions with the Same Sign on the Dynamics of the Interaction of Two Molecules with Ionic Bond

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Branching ratio of the different channels in multi-channel elementary processes is one of the most important characteristic of the molecular interactions, which is very sensitive to the topography of the potential energy surface. We report about scattering dynamics in the CsCl + RbJ system has been investigated by quasiclassical trajectory simulation in the collision energy range from 0,1 eV to 25 eV. Initial values were chosen by Monte-Carlo technique on the base of real distributions in accordance to the experimental conditions [1,2].

Potential energy surface was represented as an additive function of six pairwise potentials of the truncated Rittner form [3]:

\[ U(R) = E(R) \pm 1/R - (\alpha_1 + \alpha_2)/R^4 - C/R^6 \]  \hspace{1cm} (1)

where \( E(R) \) – repulsive energy in Born-Mayer model

\[ E(R) = A \cdot \exp(-R/\rho) \]  \hspace{1cm} (2)

Here \( \rho \) is a calibration factor \( \rho \) is so-called “hardness” parameter of a repulsive wall, \( \alpha_1 \) and \( \alpha_2 \) are polarizabilities of the two ions involved, \( R \) – dispersion constant and \( R \) – interatomic distance. Symbol “+” in Coulomb term corresponds to interaction of the ions with the same sign and symbol “-” corresponds to interaction of opposite charged ions.

Four molecular potentials describe the interaction of the ions of opposite sign and their parameters are determined from the spectrometric data with high accuracy. On the contrary the parameters of the potentials Cs\(^+\) - Rb\(^+\) and Cl\(^-\) - J\(^-\) were calculated on the base of empirical rules, and the reliability of this technique isn’t very good [4,5]. Parameter \( \rho \) in the exponential Born-Mayer term is the least reliable one. Increase of this parameter leads to decrease of the overlap of electronic clouds of two ions and increase of the minimum possible distance of approach of the ions at defined collision energy.

Interactions of two molecules with ionic bond can proceed according to following 12 channels:

1. CsCl + RbJ \( \rightarrow \) CsCl + RbJ
2. \( \rightarrow \) Cs\(^+\) + Cl\(^-\) + Rb\(^+\) + J\(^-\)
3. \( \rightarrow \) Cs\(^+\) + Cl\(^-\) + RbJ
4. \( \rightarrow \) Rb\(^+\) + J\(^-\) + CsCl
5. \( \rightarrow \) CsJ + Rb\(^+\) + Cl\(^-\)
6. \( \rightarrow \) RbCl + Cs\(^+\) + J\(^-\)
7. \( \rightarrow \) CsJ + RbCl
8. \( \rightarrow \) CsClRb\(^+\) + J\(^-\)
9. \( \rightarrow \) CsClJ\(^-\) + Rb\(^+\)
10. \( \rightarrow \) CsJRb\(^+\) + Cl\(^-\)
11. \( \rightarrow \) RbJCl\(^-\) + Cs\(^+\)
12. \( \rightarrow \) CsClRbJ
The calculations of the excitation functions have been carried for two sets of “hardness” parameters $\rho_i$ – the first time for the values from the empirical rules [5] and once again for the double values.

Channel 1 in above-mentioned scheme corresponds to the sum of elastic and inelastic scattering and hasn’t investigated in details.

Channel 2 appears for the collision energies exceeded the sum of the dissociation energies of both reacting molecules, which is near 9 eV. The shape of the excitation function for this channel doesn’t depend from the values of “hardness” parameters, and cross section increases with the growth of collision energy, but more intensive for the double set of parameters.

Channels 3 and 4 open at $E_{rel.} = 4$ eV, and their cross sections increase with the growth of collision energy, but for the double set of the “hardness” parameters this increase is faster and for the $E_{rel.} = 25$ eV the cross section for the 3 channel is 3,5 times and for the 4 channel is 2 times higher than for initial values of $\rho_i$. The threshold for the channels 5 and 6 is near 4 eV similarly, but their excitation functions have the bell-shaped form. After the doubling of “hardness” parameters the position of maximum of the excitation function for channel 5 moved from 10 eV to 13 eV and the maximum cross section increased in 5,5 times. Similarly for the channel 6 the position of maximum of the excitation function moved from 8 eV to 17 eV, but the corresponded cross section decreased in 2 times.

The most dramatic changes on doubling the “hardness” parameters occur for the excitation function of the exchange reaction in channel 7. For the initial values of $\rho_i$ the cross section of the channel has a maximum at $E_{rel.} = 0,1$ eV and then decrease smoothly with the growth of collision energy (the decrease is near 10 times for the change of collision energy from 0,1 eV to 3 eV). For the double set of $\rho_i$ the channel has a threshold near 0,5 eV, then the cross section reaches the maximum at $E_{rel.} = 3$ eV with the following decrease for the higher values of collision energy. But in this case the maximum value of cross section is smaller in 3 times in compare with the cross section for initial values of $\rho_i$ at the same collision energy $E_{rel.} = 3$ eV.

Very interesting changes have taken place in the behaviour of excitation functions of the channels 8-11 conforming to three-atomic ionic complexes formation. All excitation functions have the threshold behaviour, pass via maximum, and then cross sections decrease with the growth of collision energy. For both sets of “hardness” parameters the excitation functions for the channels 8 and 10 formations of positive signed ionic complexes reach their maximum values at the same collision energies near 4 eV. But for the double values of $\rho_i$ cross section of the channel 8 is exceeds in 7 times their value for the initial “hardness” parameters, and cross section of the channel 10 is less in 7 times in compare with initial value. Another situation is observed for the channels 9 and 11, which deal with the formation of positive ions and negatively charged ionic complexes. In outcome of the doubling of “hardness” parameters the maximum value of the cross section for the channel 9 practically hasn’t changed, but the position of a maximum of the excitation function shifted from 4 eV to 6 eV. Far more significant changes took place for the excitation function of the channel 11, namely their position of maximum shifted from 4 eV to 9 eV, and the maximum value of the cross section increased in 30 times. It’s interesting to note that as a result of the doubling of “hardness” parameters the most considerable growth of the cross section took place for the channel 10 associated with the formation of the lightest ion Cl$^-$ and heavy ionic complex CsJRb$^+$. The cross-section of a channel 9 formations mean on weight of an ion Rb$^+$ practically has not changed, and the cross sections of the channels 8 and 11, in which heavy ions J$^-$ and Cs$^+$ are derivate, hardly have decreased. Similar effect we observe for the group of channels 3-6. Cross section corresponding to the maximum of excitation function increase in a maximum degree for the channel 5 associated with the formation of two lightest
ions Rb\(^+\) and Cl\(^-\). Cross sections of the channels 3 and 4 increased to a less degree, and the cross section of the channel 6 associated with the formation of two heavy ions Cs\(^+\) and J\(^-\) and light molecule RbCl has decreased.

Considerable quantitative changes took place for the cross section of the channel 12 corresponded to formation of four-atom complex stabilised by rotation. For both sets of “hardness” parameters the excitation function is monotonically waning curve, but the cross section at E\(_{\text{rel.}}\)=0.1 eV for the double set of \(\rho\) decreased in 1000 times in compare to their value for initial set of \(\rho\).

From the calculations it’s clear that the values of the “hardness” parameters in repulsive potentials of the ion pairs with the same sign have very strong influence on the channel branching and the behaviour of separated channels. Probably it deals with the significant redistribution of the realised collision configurations and, as a consequence, some changes of kinematics and dynamics of the process.

References

Energetics of Hydrogen Abstraction in Derivatives of 2-Pyrrolidinone

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Inhibition of free-radical polymerization by molecular oxygen can dramatically decrease optimum production speeds and can affect the final surface properties of the product. In previous studies Miller and coworkers have shown that N-vinyl-2-pyrrolidinone (Figure I.) greatly increases the relative rates of acrylate polymerization in air at low light intensities. In a subsequent study, Miller and coworkers investigated other cyclic and acyclic N-vinylamides and other cyclic amides without the vinyl functional group. They found that while the cyclic N-vinylamides caused the greatest reduction in the oxygen inhibition of free-radical polymerization, all of the cyclic amides caused some reduction. They concluded that there must be something specific about the amide ring which contributes to the oxygen effects which is enhanced in the cyclic N-vinyl amides and offered a possible explanation which involves hydrogen abstraction from a carbon adjacent to the nitrogen in these cyclic amides followed by reaction of the resulting radical with oxygen.
An Efficient Parallel Algorithm for the Calculation of Canonical MP2 Energies

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We present the parallel version of a previous serial algorithm for the efficient calculation of canonical MP2 energies (P. Pulay, S. Saebo and K. Wolinski, Chem. Phys. Lett. 2001, 344, 543). It is based on the Saebo-Almlöf direct-integral transformation, coupled with an efficient prescreening of the AO integrals. The parallel algorithm avoids synchronization delays by spawning a second set of slaves during the bin-sort prior to the second half-transformation. Results are presented for systems with up to 2000 basis functions. MP2 energies for molecules with 400-500 basis functions can be routinely calculated to microhartree accuracy on a small number of processors (6-8) in a matter of minutes with modern PC-based parallel computers such as our QuantumStation™.
A 3D-QSAR pharmacophore model for chloroquine (CQ) resistance reversal ability has been developed from a training set of 17 compounds by using CATALYST. The compounds include imipramine, desipramine, and fifteen of their analogues, all of them showed CQ-resistance reversal ability of varying degrees. The IC$_{50}$ values of the training set of compounds covered activities ranging from 2.3 to 49.7 ng/ml determined against the W2 clone of Plasmodium falciparum. The generated pharmacophore model indicates that two hydrophobic interaction sites on the tricyclic ring, a ring aromatic site and a hydrogen bond acceptor site at the side chain nitrogen atom are necessary for potent activity. Stereoelectronic properties calculated by using the AM1 semi-empirical procedure are found to be consistent with the model, particularly the electrostatic potential profiles characterized by a localized negative potential region by the side chain nitrogen atom and a large region covering the aromatic ring. The calculated data further revealed that aminoalkyl substitution at the N5-position of the heterocycle and a secondary or tertiary aliphatic aminoalkyl nitrogen atom with two or three carbon bridge to the heteroaromatic nitrogen (N5) are required for potent “resistance reversal activity.” The lowest energy conformer for the seventeen structures was determined and optimized to afford stereoelectronic properties such as molecular orbital energies, electrostatic potentials, atomic charges, proton affinities, octanol-water partition coefficients (log P), and structural parameters. A fairly good correlation appears to exit between resistance reversal activity and intrinsic basicity of the nitrogen atom at the tricyclic ring system, frontier orbital energies, lipophilicity, and density of the molecules.
Molecular Modeling of Polyamino Acid Inhibitors of Clathrate Hydrates

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Clathrate hydrates are ice-like crystalline substances in which nonpolar molecules are encapsulated by network of hydrogen-bonded water molecules. In aqueous environments of specific temperature, pressure and composition, ice crystals will form “cages” that contain guest molecules. Clathrate hydrate formation can be a serious problem in natural gas and oil recovery from deep and cold deposits. Recently discovered polymeric kinetic inhibitors offer the possibility of control of hydrate formation at very low concentration, thus significantly lowering the costs of oil and gas recovery and transportation. We have synthesized and analyzed the inhibition properties of several very efficient polymeric kinetic inhibitors of clathrate hydrates. In order to optimize the inhibitory activity of kinetic inhibitors of clathrate hydrates, we have performed a molecular modeling study of binding of several polypeptide inhibitors to the (111) surface of Structure II of clathrate hydrate crystal. Polyamino acid kinetic inhibitors that included lysines, aspartic acid, alanines, and polymers with ring side chains were modeled using the Cerius² program for materials sciences. Significant insight was gained into the types of interactions and binding energies between the macromolecules and the (111) surface of Structure II of clathrate hydrates. This insight is being used to design even more efficient kinetic inhibitors of clathrate hydrates.
Quasiclassical Coherent States: Applications to State Resolved Ion-Molecule Dynamics

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A method due to Prony that fits a set of exponential curves to a time dependent signal is generalized. The Generalized Prony's (GP) method is applied to study rovibrational dynamics of molecular products obtained in non-adiabatic molecular dynamics. The dynamics is performed with classical nuclei using Electron Nuclear Dynamics (END) theory. The application of GP in an a posteriori analysis of the nuclear trajectories obtained from END gives the classical values for vibrational frequencies and amplitudes of the normal modes. The use of quasi-classical oscillator coherent states parameterized by these values yield the vibrationally state resolved cross sections. GP method is applied to END simulations of the charge transfer scattering of protons and water at 46.0 eV center of mass energy. The analysis is used to obtain vibrationally resolved cross sections, which are compared to crossed beam experimental data of Toennies, et al. (J. Toennies, et. al., J. Chem. Phys. 87(1987) 5256.) Electron Nuclear Dynamics (END) theory at its simplest level of approximation as applied to chemical reactions treats the atomic nuclei as classical particles while the electrons are represented by a simple wave function. This level of treatment is implemented in the ENDyne code, and applied to a number of reactive processes involving ion-molecule collisions. Even at this level of implementation the END theory allows non-adiabatic coupling in its dynamics and requires no potential energy surfaces. At low to intermediate collision energies reaction products as a rule do not exhibit violent rovibrational motion. A typical molecular product fragment of a chemical reaction behaves as a semi-rigid classical rotor with only a weak coupling of rotations and vibrations. Additionally, these motions follow very closely the dynamics given by the classical equations of motion. In our poster it is demonstrated that it is possible then to extract information about the participation quantum states from this classical motion. In the case of a diatomic fragment an a posteriori analysis has shown how the harmonic oscillator coherent states can be utilized to obtain a distribution of quantum vibrational states from the classical trajectory of the nuclei. We present a generalized approach for polyatomic fragments and it is applied to scattering of protons and water at a collision energy of 46 eV in the center of mass frame. In the first section a method due to Prony and discussed in the book by Marple to model sampled data as a linear combination of complex exponentials is generalized. The standard prony analysis applies to a one dimensional time series consisting of a known number of exponential signals. Here Prony's method (PM) is generalized to apply to general polyatomic systems with more degrees of freedom. In the second section we apply the Generalized Prony's Method (GPM) to ENDyne simulations of proton-water scattering. The GPM applied to the water post collision nuclear trajectories yields rovibrational parameters. These parameters are used to determine HOCS that correspond to the classical nuclear trajectory. The trajectories and rovibrational states are then uses to calculate state resolved differential cross sections. These theoretical results are then compared to the experimental results of Toennies, et. al who provided the motivation for using this system. Additionally, a set of rotational coherent states are used to calculate the rotationally resolved differential cross sections.
The Nonrigidity of the Amino Group in Cytosine, Adenine, and Guanine

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The results of an ab initio post-Hartee-Fock study of the amino group of cytosine are reported. The molecular structure and pathways have been analyzed. The geometry of the local minimum and the transition states were optimized by the gradient procedure at the MP2 and B3LYP level of theory. The optimizations were verified by the energy second derivative calculations. Two basis sets were used, the medium set: 6-31+G(d,p) and the extended set AUG-cc-pVDZ. The calculations reveal that this molecule is nonrigid in respect to the torsion and umbrella vibration of amino group. It results in a very complex picture of the amino group motion which includes tunneling and a below barrier large amplitude motion. We expect a similar nonlinear dynamic behavior for adenine and guanine.
Nucleus Independent Chemical Shift Evaluation of the Aromaticity of Pauling’s Mystery Molecule and Some of Its Derivatives


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Nucleus independent chemical shift (NICS) values were used to evaluate the aromatic character of 2-azido-5,8-dihydroxy-1,3,4,6,7,9,9b-heptaazaphenalene 1 known as Pauling’s Mystery Molecule (PMM). The 2-nitrene derivative 2, (both singlet and triplet), and 2-hydroxy derivative 3 of PMM were also examined. Tri-s-azine, the core ring system, served as a reference molecule for evaluating aromaticity. Geometries were optimized at the B3LYP/6-31g(d,p) level while NICS values were calculated at the same level using the gauge invariant atomic orbital (GIAO) approach. Both 1 and 3 have planar minima but 2 was found to be nonplanar.
QR-SC-MEH-MO Calculations on the Electronic Structure and Bonding in the Nd₂ Molecule

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The Nd₂ molecule is interesting, in that the only reported data about it is a published report more than twenty-five years ago, relating a bond dissociation energy less than 1.7 eV [1]. There does not appear to be any other experimental or computational data on this molecule. Calculations of the electronic structure and bonding in the Nd₂ molecule, have been carried out via the QR-SC-MEH-MO (quasirelationistic self-consistent modified extended Huckel molecular orbital) method [2]. Most recently, similar calculations were completed on the Cr₂ and MO₂ molecules, which provided conformation of antiferromagnetic coupling (essentially in Cr₂) as the primary bonding factor [3].

It appears from the results obtained for Nd₂, that the highest occupied MOs are open shells having almost total 4f orbital character. An analysis of spin pairing and spin orbit interactions implies the possibility of spin coupling between 4f electrons. If this is actually the case, then this would be the first report of any formal 4f-4f covalent bond in any substance.

Details of the data in terms of bonding options and an evaluation of the bond dissociation energy will be reported.

References

Molecular Dynamics Simulations of RDX systems

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We are reporting on molecular dynamics simulations of crystalline RDX, which are performed with the goal to study the role of defects in detonation initiation processes. The development of the intra- and intermolecular potential is the focus of this presentation. The size of the molecule as well as the symmetry properties of the crystal make it necessary to assume united-atom potentials for the Van-der-Waals and electrostatic interactions. For the intramolecular forcefield, we introduced novel approaches for the side group conformational stages, as well as hydrogen bridges within the molecule. The process of finding a viable intermolecular potential is ongoing. We present our most promising potentials.
Identifying Reactive Portions of Molecules 
by Segmental Analysis 
of Surface Electrostatic Potentials

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Noncovalent interactions are predominantly electrostatic in nature. An effective tool for their investigation and elucidation is the electrostatic potential on the molecular surface. In the past, we have shown that a variety of condensed phase macroscopic properties can be expressed in terms of site-specific and global statistical quantities that characterize the overall pattern of the surface potential. Since then, we have extended our approach to interactions in biological systems. We have recently presented quantitative treatments of the anti-HIV activities of three groups of reverse transcriptase inhibitors, in which statistical quantities describing the entire drug molecule were used in the correlations. In this poster, we are exploring a new approach, the use of segmental analysis of surface potentials to both identify reactive portions of molecules and to obtain quantitative correlations with anti-HIV activities. We will present our results for two groups of reverse transcriptase inhibitors (carboxanilides and aminoguanidines) and one group of non-peptidic protease inhibitors (cyclic cyanoguanidines).
Accuracy Studies of a Parallel Algorithm for Solving the Hydrodynamic Formulation of the Time-Dependent Schrödinger Equation

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This work examines the accuracy of a parallel moving least squares algorithm for solving the governing equations of the hydrodynamic formulation of quantum mechanics. The algorithm employs a quantum trajectory method based on the serial algorithm introduced by Wyatt and Lopreore [5] and solves the associated linear least squares problems using either normal equations, QR factorization, or singular value decomposition (SVD). The presentation will discuss the accuracy of the algorithm when using each of these methods for both the free particle and the harmonic oscillator, and the results of a series of experiments designed to determine the spatial and temporal dependence of each of these accuracies will be presented.

Introduction

Wave-packet methods are an important tool in the calculation of time-dependent quantum-mechanical effects in many areas of physics and chemistry. When employing time-dependent wave-packet methods, computational analysis is closely related to experimental laboratory methods, and the resulting wave functions are both normalizable and defined in standard Hilbert space. Further, quantum-mechanical systems in external fields can be directly treated when using a time-dependent wave-packet method. While these advantages make wave-packet methods useful for modeling many types of quantum systems, such methods are most often used to compute the solution to the time-dependent Schrödinger equation (TDSE) (1) to determine the dynamics of quantum-mechanical systems composed of a single particle of mass \( m \) moving in a potential \( V \). The system wave function \( \Psi \) is a function of time \( t \) and position \( \vec{r} \) that can be decomposed into polar form (2) with real-valued amplitude \( R \) and phase \( S \).

\[
\frac{i\hbar}{\partial t}\Psi = \hat{H}\Psi, \quad \hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V
\]

\[
\Psi(\vec{r},t) = R(\vec{r},t)\exp[iS(\vec{r},t)]
\]

The interpretation of quantum mechanics suggested by Bohm in 1952 [1,2] leads to a wave-packet representation of quantum systems. The Bohmian theory, as it is now termed [3,4], is of great interest from a computational perspective [3,5,6,7,8,9,10]. The Bohmian interpretation leads to a formulation of the TDSE with a system of governing equations resembling the formulation of a hydrodynamic fluid mechanics problem [5,8]; as such, this formulation of quantum mechanics is sometimes referred to as quantum fluid dynamics (QFD). When the equations of QFD are cast in a Lagrangian framework [11,12,13,14], the resulting equations resemble the classical form of Newton’s second law and the continuity equation [5,8].

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The Lagrangian formulation of QFD is solved using a moving frame that centers on each member of a set of pseudoparticles (also referred to as quantum subparticles or fluid mass points). These pseudoparticles are deployed to form an adaptive grid that tracks the state of the system [8]. This approach leads to a computational problem that is easily decomposed for parallel processing. The Lagrangian equations of QFD, assuming that $H$ is independent of time and that all units are expressed in atomic units, are found in (3) (expressed in terms of the definitions in (4)).

\[ m \frac{d}{dt} \vec{v} = -\vec{\nabla}(V + Q) = \vec{f}_c + \vec{f}_q \]  
\[ \frac{d}{dt} \rho = -\rho \vec{\nabla} \cdot \vec{v} \]  
\[ \vec{f}_c \equiv -\vec{\nabla}V \] (classical force)  
\[ \vec{f}_q \equiv -\vec{\nabla}Q \] (quantum force)  
\[ \rho \equiv R^2 \] (probability density)  
\[ \vec{v} \equiv \frac{1}{m} \vec{\nabla}S \] (velocity)  
\[ Q \equiv -\frac{1}{2m} \frac{1}{\rho^{1/2}} \frac{1}{\rho^{1/2}} \] (quantum potential)

**Algorithm**

The parallel algorithm for solving the hydrodynamic formulation of the time-dependent Schrödinger equation is based on the serial algorithm introduced by Wyatt and Lopreore [5,15]. The algorithm solves the one-dimensional Lagrangian equations of QFD using a moving least squares (MLS) method with explicit update. The algorithm tracks the state of the system through the probability density $\rho$. The probability density $\rho$ is updated explicitly using the density update equation.

\[ \rho(\vec{r}, t + dt) = \rho(\vec{r}, t) \exp(-dt \vec{\nabla} \cdot \vec{v}), \]  

which is obtained by integrating the second equation of (3). All function values required to compute the updated value of $\rho$ are obtained using the MLS method.

In the MLS method, each function $f$ that is required to update the state of the system is assumed to be defined on an unstructured set $A = \{x_i : 1 \leq i \leq n\}$ of $n$ points defined by the positions of the $n$ pseudoparticles that are deployed to track the state of the system. The objective of the MLS method is to find an approximate value for $f$ in the neighborhood of each $x_i$. Two integers $N_b$ and $N_p$ are selected such that $N_b < N_p$, and a set of local polynomials, $P = \{p_i : 1 \leq i \leq N_b\}$, is defined by $p_i(x) = x^{i-1}/(i-1)!$ in order to make an expansion $f_i$ of $f$ around each $x_i$ as defined by

\[ f_i(x) = \sum_{j=1}^{N_b} a_j p_j(x - x_i) : a_j \in (-\infty, \infty). \]  

For each $x_i$, a set $S$ is defined by selecting $x_i$ and the $N_p-1$ points in $A$ other than $x_i$ that are closest to $x_i$. The approximation $f_i$ is applied at each point in $S$ to obtain a system of $N_p$ linear equations. These equations are then solved as an over-determined weighted linear least squares problem using either normal equations, QR factorization, or singular value decomposition (SVD) to obtain the value of each $a_j$. The approximate value of $f(x_i)$ as represented by $f_i(x_i)$ can then be computed directly using the approximating sum [5,16,17].
The parallel algorithm is implemented as an explicit update loop that iterates across the problem time steps. Within each update, a main computational loop iterates across the problem pseudoparticles. This main computational loop is parallelized by using the OpenMP API [18] to distribute the computations of several subloops across all available processors. An outline of the parallel algorithm and further information regarding the implementation of the algorithm is presented in the presentation.

Accuracy

The presentation discusses the accuracy of the parallel MLS algorithm for solving the hydrodynamic formulation of the TDSE. Applications of the algorithm to the free particle and the harmonic oscillator are examined. In each case, the accuracies of the algorithm while employing normal equations, QR factorization, and singular value decomposition are presented. The results of a series of experiments designed to determine the spatial and temporal dependence of the measured accuracies are also presented.

References


URL: http://www.openmp.org/specs/.
Conformational Study of 1, 2 Cycloundecadiene

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1, 2 - Cycloundecadiene was synthesized from a mixture of cis and trans cyclodecenes by known procedures. A two percent solution of the compound in propane was studied by low - temperature $^{13}$C NMR spectroscopy. A total of 17 peaks were observed at -166.7 °C, corresponding to two conformations of similar populations, one of $C_1$ symmetry (11 peaks) and the other of $C_2$ symmetry. The line shapes indicate that exchange of sites for the CH and CH$_2$ carbons of the $C_1$ conformation does not take place by the way of the $C_2$ conformation. The NMR results for this compound will be discussed in terms of the conformations predicted by molecular mechanics calculations obtained with the Merck force field. Ab initio calculations of free energies are also being done at the HF/6-31+G* level for 12 conformations. Rate constants and barriers are being determined from the NMR spectra and will be reported. This work was supported by NSF - CREST Grant No. HRD - 980 5465.
Structural Characterization of MAO and Related Aluminum Complexes. Solid-State $^{27}$Al NMR with Comparison to EFG Tensors from ab initio Molecular Orbital Calculations

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The experimental $^{27}$Al NMR spectrum of methyl aluminum oxane (MAO, a new generation co-catalyst used in polyolefin production) is compared to spectra resulting from ab initio calculations of $^{27}$Al quadrupolar coupling constants and asymmetry parameters for several models for MAO. Geometry optimized ROHF calculations using the cc-pVDZ basis set are used to assess the different models. The best agreement between experiment and theory is obtained for two cage compounds based on the well-known Barron models for MAO.
The Influence of Square-Planar Platinum Complexes on DNA Base Pairing. An ab initio DFT Study

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The energetics and structures of Watson-Crick DNA base pairs guanine/cytosine and adenine/thymine metalated by the square planar platinum adducts trans-PtCl2(NH3), trans-PtCl(NH3)2+, and Pt(NH3)32+ at the N7 purine position have been investigated using quantum chemical methods. The platinated complexes were optimized using Becke3LYP density functional theory (DFT) approach. For each base pair two kinds of structures were evaluated. One of them keeping C5 point group of symmetry and the other without any geometrical restrictions. In the later case system forms an intrasystem H-bonds between the ligands attached to the metal and the exocyclic 6-position of the purine nucleobase. Interaction energies were evaluated and decomposed into individual pairwise and many-body terms. For some systems, the DFT approach provided biased interaction energy decomposition when including the correction for the basis set superposition error. Thus, these systems were re-evaluated with a second-order Møller-Plesset (MP2) perturbation approach resulting in correct decomposition. The calculations show, among other results, that the GC base pair is significantly strengthened by polarisation effects when Pt(NH3)32+ is bound to its N7 position. This observation is in agreement with recent solution experiments on platinated base pairs. The calculations suggest that the effect exerted by Pt(NH3)32+ on the base pair stability is larger compared with the effect exerted by inner-shell binding of hydrated divalent cations of zinc and magnesium groups.
Electron-Nuclear Dynamics Study for Protons Colliding with Ethane for Intermediate Projectile Energies: Preliminary Results

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We use the Electron-Nuclear Dynamics theory to study the stopping, charge exchange, and differential cross sections for proton projectiles colliding with ethylene in the gas phase for projectile energies ranging from 200 eV/amu to 25 keV/amu. We present results for the deflection function, semiclassical correction to the direct differential cross section, charge exchange probabilities, total charge exchange cross section, electronic, nuclear and rovibrational energy loss, and stopping cross sections. We also analyze some chemical reactions, as for example, \( \text{H}^{+} + \text{C}_2\text{H}_6 \rightarrow \text{H}^{*} + 2\text{CH}_3 \) and \( \text{H}^{+} + \text{C}_2\text{H}_6 \rightarrow \text{H}^{*} + \text{CH}_3 + 3\text{H}^{*} \) which occurs for some impact parameters, orientations and projectile energies. The results show good agreement with available experimental data.

References

Conformational Study of Formic Acid by Dynamic NMR Spectroscopy

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Low-temperature $^1$H NMR spectra at 300.52 MHz of a solution containing 2% formic acid and 3% hexafluoroacetone in 3:1:1 CHClF$_2$, CHCl$_2$F, dimethyl ether show peaks at δ 11.77 and 12.22 at -107 °C for the OH protons of the Z and E conformations, and integration of this spectrum gives populations of 0.938 and 0.062. Coalescence was observed at -90.3 °C. The $^{13}$C NMR spectrum also shows peaks for Z and E isomers, which appear at δ 165.06 and 164.46. From the population of 0.062 for the E-isomer at -107.0 °C, the percentage for this conformation of formic acid at -90.3 °C was estimated to be 7.8% with the assumption that the E-Z free-energy difference remains constant. Rate constants of 259 and 22 s$^{-1}$ at -90.3 °C were estimated by lineshape matching for the E-to-Z and Z-to-E conversions. Because interconversion may actually be taking place by intermolecular hydrogen exchange, the calculated free-energy barriers of 8.5 and 9.4 kcal/mol are lower limits for the barriers to rotation about the C-OH bonds. For comparison, the free-energy barriers for methyl formate in 1:1 acetone-$d_6$/DMF are 9.85 and 11.91 kcal/mol, and the population for the E-isomer of this ester at -82.5 °C in 3:1:1 CHClF$_2$, CHCl$_2$F, dimethyl ether is 0.002 ± 0.001. The finding of a larger population for the E-isomer of formic acid than for methyl formate indicates that the relative populations are not determined by steric effects. Further studies on carboxylic acids are in progress. This work was supported by NIH-MBRS Grant No. GM08047.
Quadratic MCSCF Algorithm for the Polarizable Continuum Model

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We present a new formulation of the optimization of a multiconfigurational (MCSCF) wavefunction for a molecular solute described by the Polarizable Continuum Model. The new algorithm is based on an exponential parametrization of both orbital and configurational parts, and exploit the second-quantization formulation of the nonlinear electronic Hamiltonian of the solute. The MCSCF equations are solved by using a second order method with quadratically convergence properties. Numerical application regarding the solvent effects on the electronic structure of 1-3 dipole systems, and on the excitation energy of a merocyanine is given.
Linear and Nonlinear Optical Properties of Pyridine N-Oxide

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In the search for new materials with exceptional linear and nonlinear optical properties, the electronic properties of pyridine N-Oxide molecule have been investigated by Ab Initio and Density Functional Methods DFT. In this investigation was studied the static and dynamic polarizabilities of the pyridine N-oxide molecule using the computational methods of the quantum mechanics. The static properties were evaluated with the Ab initio (Hartree-Fock: HF, Møller-plesset at MP2 levels of theory) and Density Functional Theory DFT at BLYP and B3LYP levels, and the Gaussian 98 software, with the STO/6-31+G(d,p), STO/6-311+G(3d,3p) and STO/6-311++G(3d,3p) basis sets. The dynamic properties were calculated with the Time Dependent Hartree-Fock method TDHF implemented in the GAMESS computational program and using the STO/6-31+G(d,p) basis set.

We found that the link between the N-O bond with the highly anisotropic pyridine ring leads to a structure that shows amplified optical response with regard to pyridine molecule.
DFT and EPR Study of Uracil and Thymine Radical Anions

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Lu and co-workers have reported in situ photolytic experiments which produce reduction products in pyrimidine bases (1). In this article there is discussion of several non-planar radicals. The authors calculated spin densities and isotropic hyperfine couplings of the pyrimidine base reduction products by Density Functional Theory to support these non-planar assignments. These conclusions are however at odds with what is observed when these same radicals are produced in the solid state.

The radicals reported by Lu et al. have been observed in irradiated single crystals and studied by detailed EPR/ENDOR experiments (2). In these studies there is ample evidence that most of the radicals observed are planar. Typical results for the thymine anion observed in irradiated single crystals of thymine monohydrate (3) are shown in Table I. The direction of \( A_{\text{min}} \) (Table I) is known the be associated with the direction of the \( \text{C}-\text{H} \) bond, while the direction associated with the \( A_{\text{mid}} \) indicates the direction of the p-electron orbital. These directions are easily calculated for the crystal structure (4), and are included in Table I. One sees that the direction associated with \( A_{\text{mid}} \) deviates only 1.1° from the computed perpendicular to the ring plane (the direction of the p-orbital), while the direction of \( A_{\text{min}} \), deviates only 2.5° from the computed direction of the C6-H bond. This is very clear evidence that the radical shown here is planar in the solid state.

Lu and co-workers report reduction products in uracil. The \( \text{C6-H}_a \) hyperfine coupling tensors for two uracil anions determined from irradiated single crystals are listed in Table I (5, 6). One notes that the agreement between experimental direction cosines and the directions of the ring perpendicular and C6-H bond directions indicate that these radical sites are essentially planar also. Lu et al.(1) report the C6-H\(_{a}\) isotropic hyperfine coupling is -35.10 MHz for the uracil anion, which agree well with the results obtained from detailed EPR/ENDOR experiments on a single crystal of 5'UMP (Table I).

Lu et al.(1) report DFT calculations on several reduction products. The uracil anion is shown to have a fairly large C6-H\(_{a}\) hyperfine coupling (-48 MHz) when the C6-H proton is in the ring plane. The calculations performed by Lu et al.(1) involve optimizations with B3LYP and MP2 on 6-31 G(d) basis sets followed by hyperfine coupling calculations at the B3LYP/6-31 G(d) level. If one computes the hyperfine couplings for the uracil anion at a higher level (B3LYP/6-311+G(2df,p)) on the optimized structure of 1-Methyl Uracil (1-MU)(7), the C6-H\(_a\) isotropic hyperfine coupling is -40.43 MHz, which is close to the experimental values listed in Table I for the 1-MU anion observed in the single crystal of 1-MethylUracil:9-EthylAdenine (MUEA).

It is important to realize that in the solid-state it is rare to observe charged radicals. Most reduction products observed in pyrimidines in the solid state are actually protonated anions (2). Calculations performed on the \( \text{C4-OH} \) protonated anion of 1-MU lead to a C6-H\(_a\) isotropic hyperfine coupling is -41.87 MHz, again close to the experimental value.

Calculations on both the native anion and the C4-OH protonated anion in 1-MU produce reasonable agreement with the experimental results obtained from planar radicals in the solid-state. The second entry in Table I is the uracil anion observed in 5'-UMP. Here the C6-H\(_a\) hyperfine coupling is -36.1 MHz, lower than in 1-MU, and more like the uracil reported by Lu et al.(1) (-35.1 MHz). Lu et al.(1) contend that the C4-C5-C6-H torsion angle must be \(-10^\circ\) to
reduce the C6-Ha coupling ca. -35 MHz. However, performing these same calculations with the extended basis sets (B3LYP/6-311+G(2df,p)), it can be seen that this torsion angle needs to be less than 5° (see Table II).

Lu et al. (1) have also examined thymine anions. In solution the C6-Ha isotropic hyperfine coupling is observed to be -33.00 MHz. This agrees almost exactly with the results in the solid state for thymidine (Table I). Theoretical calculations performed on the thymine anion are presented in Table II. While these results are similar to those discussed above for the uracil anion, there are some significant differences. As with uracil, the planar thymine anion is not the minimum energy configuration (as previously noted by Wetmore et al.(8)), and the computed C6-Ha isotropic hyperfine coupling is too large. A search for the energy minimum produced a C6-Ha proton ca. 23° out of the plane. Unlike the case for uracil, the C6-Ha hyperfine coupling dropped to zero and then reaches a positive value of about 5 MHz. This means there is a change in the orbital of the unpaired electron. As a p-radical bends, the Aiso(Ha) would change from a negative value to large positive values which are characteristic of s-radicals in which the unpaired spin is in an orbital possessing significant s-character.

For the reduction product observed in thymidine in the solid state, the electron adduct is protonated at C4=O. DFT calculations on the protonated thymine anion with the C4-OH proton in the molecular plane yield a C6-Ha isotropic hyperfine coupling of -40.1 MHz. As with the uracil case, it seems as if the native anion and the C4=O protonated anion in thymine are indistinguishable at this level of theory.

In conclusion, it has been shown that calculations using higher order basis sets appreciably lower the C6-Ha isotropic hyperfine coupling of the thymine and uracil anions. Protonation of the thymine or uracil anions at C4=O doesn’t seem to affect this coupling. It appears as is a slight bending of the anion radical (less than 5° at the radical site) may be necessary to reproduce the experimentally observed C6-Ha isotropic hyperfine coupling.

This work is supported by PHS Grant R01 CA36810-14 awarded by the National Cancer Institute, DHHS.

References
Table I: Hyperfine Coupling Parameters for Pyrimidine Anions

<table>
<thead>
<tr>
<th>Coupling</th>
<th>Principal Values</th>
<th>Isotropic Value</th>
<th>Dipolar Values</th>
<th>Direction Cosines</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td>&lt;a&gt;</td>
<td>&lt;b&gt;</td>
</tr>
<tr>
<td>Thymidine</td>
<td>-55.7</td>
<td>-22.6</td>
<td>0.732</td>
<td>0.656</td>
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<tr>
<td>C6-H&lt;sub&gt;a&lt;/sub&gt;</td>
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<td>3.2</td>
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<td>-13.2</td>
<td>20.3</td>
<td>0.048</td>
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</tr>
<tr>
<td>5'-UMP</td>
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<td>-23.0</td>
<td>0.765</td>
<td>0.464</td>
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<tr>
<td>C6-H&lt;sub&gt;a&lt;/sub&gt;</td>
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<td>-36.1</td>
<td>3.2</td>
<td>-0.027</td>
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<td>-39.1</td>
<td>3.8</td>
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<td></td>
<td>-22.2</td>
<td>16.9</td>
<td>-0.024</td>
<td>0.160</td>
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</tbody>
</table>

All hyperfine couplings in MHz.

<sup>a</sup>See refs. (3) and (4).
<sup>b</sup>Angle that the direction of \( A_{\text{mid}} \) makes with the perpendicular to the ring plane is 1.1°.
<sup>c</sup>Angle that the direction of \( A_{\text{min}} \) makes with the C6-H bond direction is 2.5°.
<sup>d</sup>See refs. (5) and (9).
<sup>e</sup>Angle that the direction of \( A_{\text{mid}} \) makes with the perpendicular to the ring plane is 7.1°.
<sup>f</sup>Angle that the direction of \( A_{\text{min}} \) makes with the C6-H bond direction is 4.0°.
<sup>g</sup>See refs. (6) and (10).
<sup>h</sup>Angle that the direction of \( A_{\text{mid}} \) makes with the perpendicular to the ring plane is 12.2°.
<sup>i</sup>Angle that the direction of \( A_{\text{min}} \) makes with the C6-H bond direction is 6.1°.
Cis-diamminedichloronickel and its Interaction with Guanine and Guanine-Cytosine Base Pair*

Kristy Cochran, Gareth Forde, Glake A. Hill, Leonid Gorb, and Jerzy Leszczynski

Computational Center for Molecular Structure and Interactions
Department of Chemistry, Jackson State University

Comprehensive ab initio calculations are performed on Cis-diamminedichloronickel (cisni) at the HF, DFT, and MP2 levels of theory. The results are compared to those obtained for cisplatin. The characteristics of the interactions of cisni with Guanine and Guanine-Cytosine base pair are also evaluated and compared to the interactions of cisplatin. Cisni causes similar geometric changes of the base as cis-platinum when complexed to guanine. The palladium and platinum complexes also show similar characteristics when complexed to GC base pair. However, this study revealed higher dissociation energy of the chlorine ligands that indicate areas of differences between the title Ni and Pt and Pd complexes. Similar interaction energy of the cispd with guanine to that of cispt indicates areas of differences between the title Ni and Pd complexes.
Mechanistic Interpretation for the Exchange and Abstraction Reactions of NH$_3^+$ + D$_2$ at Hyper Thermal Energies

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Quantum Theory Project, Department of Chemistry and Physics University of Florida Gainesville, Florida 32611-8435

Minimal Electron Nuclear Dynamics (END) theory is applied to the NH$_3^+$ + D$_2$ reaction at collision energies from 6 to 16 eV in the center of mass frame. This method for direct nonadiabatic dynamics describes the electrons with a family of complex determinantal wavefunctions in terms of non-orthogonal spin orbitals and treats the nuclei as classical particles. There are no geometrical constraints imposed on this six-atom system.

Our results explain recent experimental data by Poutsma et al. [1] and suggests a unified interpretation for the whole class of reactive collision experiments performed on NH$_3^+$ + D$_2$. Results for total cross sections as well as velocity-angle distributions for the abstraction and exchange channels were computed and are discussed.

References

An ab Initio Study of Hydrogen Bonding Effects on the $^{15}$N and $^1$H Chemical Shielding Tensors in the Wobble Base Pairs of Nucleic Acids

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The wobble base pairs (i.e., guanine–thymine, guanine–uracil, and cytosine–adenine+) comprise more than half of the non-Watson–Crick base pairs and mismatches in a large set of known secondary structures of nucleic acids [1]. To stipulate NMR spectroscopic investigations of the wobble pairs dynamics, the detailed analysis of the magnitudes and the spatial orientation of the chemical shielding tensors of the imino $^{15}$N and $^1$H nuclei (N1 – H1 of guanine and N3 – H3 of thymine/uracil) has been performed adopting the approach described in the references [2] and [3]. A thorough comparison between chemical shielding of different geometrical arrangements of wobble pairs [4], and between Watson–Crick and wobble pairing schemes, will be presented. For these bonding situations, the differences in the response of respective $^{15}$N and $^1$H chemical shielding tensors to the hydrogen bond length will be documented. The data will be discussed in the context of several approaches of relaxation control in NMR experiments [5].

Acknowledgement. This research has been supported by the Grant Agency of the Czech Republic (Grants 203/99/0311 and 203/99/0576) and by the Ministry of Education of the Czech Republic (Grants VS96095 and J07/98:143100005). Time allocation in the Czech Academic Supercomputer Centre is gratefully acknowledged.

References:
Calculations of Static and Dynamic Hyperpolarizabilities of Benzoxazoles and Pyrazoles Structures. Correlations with Second Harmonic Generation Experimental Results.

Y. DAOUDI, P. J. BONIFASSI

*a) Institut de chimie industrielle, Université des Sciences et de la Technologie Houari Boumédiène, Bab Ezzouar, Alger, Algérie. b) Laboratoire de synthèse organique, Faculté des sciences, Université du Maine, Avenue Olivier Messiaen, Le Mans, 72017, France*

**INTRODUCTION**

Organic materials with polarized conjugated systems have attracted increasing interest because of their second-order nonlinear optical properties and have stimulated considerable research activities. Indeed, the development of new services of optical communication and integrated optics needs the production of materials possessing good non linear optical properties.

In this work we study different monomers of Pushpull conjugated molecules grafted on polystyrene or methacrylate in order to evaluate the nonlinear optical properties of these poled polymer.

**GENERAL RELATIONSHIPS FOR ELECTRICAL SUSCEPTIBILITIES AND HYPERPOLARIZABILITIES. SECOND HARMONIC GENERATION.**

The $n$th order macroscopic electric susceptibilities $\chi^{(n)}$ that relate components of the polarization to the applied field are therefore $(n+1)$-order tensors. Also, the induced polarization $P_I$ which appears when an electric field $\vec{E}$ of a laser beam interacts with material is given, as often evaluated in theoretical chemistry in different unit systems by

$$P_I = \varepsilon_0 \left( \sum_J \chi^{(1)}_{IJ} E_J + \frac{1}{2} \sum_{J,K} \chi^{(2)}_{IJK} E_J E_K + \frac{1}{6} \sum_{J,K,L} \chi^{(3)}_{IJKL} E_J E_K E_L \right) + \ldots$$

where the indices $I, J, K$ and $L$ run over the macroscopic axes of the material.

The coefficients $\chi^{(i)}$ are the electrical susceptibilities: linear for $i=1$ whose molecular equivalent is the two rank tensor, non linear for $i=2$ whose molecular equivalent is the third rank tensor, non linear for $i=3$ whose molecular equivalent is the four rank tensor.

The nonlinearities were obtained via second harmonic generation by transmission through the guiding layers in flight mode (or substrate mode) by Maker fringes technique [1]. When an intense laser light at frequency $\omega$ propagates in a nonlinear medium, the electric field generates a nonlinear polarization that gives rise to harmonic components at frequencies $2\omega, 3\omega, \ldots$ and several nonlinear effects. In the case of materials with second-order nonlinearities, we can detect in the transmitted light a component at frequency $2\omega$ that depends on the incidence angle and light polarization. The nonlinear macroscopic polarization components for the second harmonic generation in terms of the electric field can be written as:

$$P_{I}^{NL}(\omega) = \varepsilon_0 \sum_{J,K} \chi^2_{IJK}(-2\omega;\omega,\omega) F_J(\omega) F_K(\omega)$$

$$= \varepsilon_0 \sum_{J,K} d_{IJK}(-2\omega;\omega,\omega) F_J(\omega) F_K(\omega) \quad \text{in the MKS system}$$

$$P_{I}^{NL}(\omega) = \frac{1}{2} \sum_{J,K} \chi^2_{IJK}(-2\omega;\omega,\omega) F_J(\omega) F_K(\omega) \quad \text{in the gaussian system}$$
RELATION BETWEEN MATERIAL MACROSCOPIC SYSTEM AND MOLECULAR MICROSCOPIC SYSTEM.

There is no simple connection between the macroscopic $d_{33}$ coefficient obtained by EFISH and the microscopic hyperpolarizability $\beta_{ijk}$.

If $i, j, k$ are the microscopic molecular axes and $I, J, K$ the macroscopic axes, for example $K$ is the poling direction (axis OZ) and $k$ the direction Oz of molecular dipole moment in the experiment.

- $\theta_{il}$ is the angle between microscopic axis $i$ and macroscopic axis $I$.
- $\theta_{lj}$ is the angle between microscopic axis $j$ and macroscopic axis $J$.
- $\theta_{kK}$ is the angle between microscopic axis $k$ and macroscopic axis $K$.

These angles are orientation factors which provide the projections from the $i,j,k$ system axis onto $I, J, K$ system axis. The second order nonlinear coefficient $d_{ijk}$ is connected to $\beta_{ijk}$ by the expression below:

$$d_{ijk} = \left(-\frac{4}{n_I^2 n_J^2 n_K^2}\right) \left(\frac{N}{V}\right) f_\omega^2 f_{2\omega} \sum_{ijk} \cos \theta_{il} \cos \theta_{lj} \cos \theta_{kK} \beta_{ijk} = \frac{1}{2} \chi^2_{IIJK} (-2\omega; \omega, \omega)$$

- $f_\omega$ is the local field factor at the optical frequency $\omega$ of the incident beam of the laser Nd-YAg ($\lambda = 1064nm$).
- $f_{2\omega}$ is the local field factor at the angular frequency of second harmonic ($\lambda = 532nm$).
- $\beta_{ijk}$ is the microscopic hyperpolarizability of first order and frequency dependent.

$N/V$ is the number of chromophores or dye molecules per unit volume in the thin polymer film poled with a static field before the SHG experiment.

MOLECULES STUDIED and STRATEGY of CALCULATION.

The molecules studied are shown in the figure 1. The molecular microscopic hyperpolarizabilities are computed on frozen DFT (2,3) geometries with AM1 parameters (4) by TDHF theory (5) with Mopac93 program. The DFT and semi-empiric geometries are obtained with the Spartan program (Wavefunction, Inc., (1997), version5). The dynamic microscopic molecular hyperpolarizabilities are obtained with the TDHF version of Mopac (Mopac 93 Fujitsu limited) and the static values are similar with Mopac93 to very low energy value(0.0001eV) and with Mopac6 by finite field theory (6) if the electric field is 0.001AU.

RESULTS and DISCUSSION.

If we consider the tables 1 and 2, we obtain a reasonable correlation between the $d_{33}$ experiment results and the microscopic molecular first order hyperpolarizability because we find: $\beta$ for mol > $\beta_{BZFF}$ > $\beta_{BZFS}$ > $\beta_{BZX1}$ > $\beta_{BZPYR}$ for these 4 molecules with the same order for $d_{33}$: $d_{33}(BZFF)$ > $d_{33}(BZFS)$ > $d_{33}(BZX1)$ > $d_{33}(BZPYR)$. But we have and $d_{33}(BZX1)$ > $d_{33}(BZX2)$ and $\beta_{BZX2}$ > $\beta_{BZX1}$ and this is a problem because NO2 acceptor group must give larger values when we change NO2 group with CN acceptor group. We think that the parameters seen in section 3 are different between these 2 structures.

ACKNOWLEDGEMENTS

It is a pleasure to acknowledge assistance from P.Delage and S.Bourdais for access to the computing facilities.

REFERENCES

**SHG CALCULATIONS : SECOND HARMONIC GENERATION CALCULATIONS**

**TABLE 1**

<table>
<thead>
<tr>
<th>molecule</th>
<th>energy for the incident beam of the laser</th>
<th>Experimental measure of d33 coefficient in pm/V</th>
<th>dynamic hyperpolarizability value for incident energy of beam laser</th>
<th>hyperpolarizability value for a very low energy (0.0001eV) (Static value)</th>
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<tbody>
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<td>22.1</td>
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**TABLE 2**

<table>
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<th>molecule</th>
<th>dynamic hyperpolarizability</th>
<th>hyperpolarizability value for a very low energy (0.0001eV) (Static value)</th>
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<tr>
<td></td>
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<td>βo</td>
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<tr>
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<td>atomic unit 10-30esu</td>
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<td>15689</td>
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<td>2536</td>
</tr>
</tbody>
</table>

References for BZX1, BZX2, BZFF and BZFS structures:

Reference for BZPYR structure:
The Cope Rearrangement in Theoretical Retrospect

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Department of Chemistry, Indiana University
800 East Kirkwood Avenue, Bloomington, IN 47405-7102

This critical review highlights intricacies of the computational study of the Cope rearrangement of 1,5-hexadiene and its derivatives. It is demonstrated that a realistic potential energy surface in the transition region can be obtained only at very high levels of approximation. The emphasis is on the reasons why some generally reliable methods fail to make even qualitatively correct predictions about this reaction.
Are Multiconfiguration Wavefunctions Necessary to Describe Isomerization Pathways for Small Hydrocarbons?

Steven Davis and Changyong Qin

Department of Chemistry, University of Mississippi, University, MS 38677

The isomerization of tricyclo[2.1.0.0\(^4,7\)]pentane (TCP) to 1,3-cyclopentadiene (CPD) was studied using ab initio calculations at the MCSCF, MP2, and B3LYP levels of theory. Single point energy calculations were also performed using the MCQDPT2 and CCSD(T) methods. The isomerization process was found to proceed directly through a concerted, nonsynchronous pathway resulting from the opening of the bicyclobutane moiety, with an activation energy of 44.2 kcal/mol at the MCQDPT2/6-31G(d,p) level. This is in contrast to the analogous isomerization of tricyclo[3.1.0.0\(^2,6\)]hexane which occurs through an (E,Z)-1,3-cyclohexadiene intermediate. The E,Z-diene structure for the five-membered ring is too strained to be a minimum on the potential energy surface. The six-membered ring has only a shallow minimum with an activation energy for the E,Z to the Z,Z isomerization of 3.1 kcal/mol. The transition state for the TCP --> CPD reaction could not be located at the MP2 of B3LYP levels and we believe a MCSCF method is necessary to describe the reaction properly. However, the transition state for the first step of the six-carbon structure can be described by both single and multiconfiguration methods.
Model Calculations of a Supramolecular Complex of a Carbon Nanotube Bundle with Hydrogen Molecules

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Hydrogen storage is one of the prospective applications of carbon nanotubes [1]. Hydrogen molecules can not only be inserted inside nanotubes but they also can be adsorbed on the nanotube surfaces. Quantum calculations have been applied to study some nanotubes with hydrogen [2]. Such methods can be used to analyse hydrogen absorption at high temperatures or electrochemically (involving CH bond formation) but they are not appropriate for the study of physisorption inside the tubes or in the interstitial channels between them. Model calculations of physisorption were also carried out using Monte Carlo Dynamic Simulations [3-7] using Lennard-Jones potentials for describing of the nonbonding interactions but they concern mostly armchair nanotubes and treat hydrogen molecules as spheres.

Molecular mechanics, MM, calculations [8] carried out earlier [9] for an armchair (5,5)nanotube with 220 atoms (with the diameter corresponding to that of C$_{60}$) revealed that 12 hydrogen molecules placed near the open end of this nanotube were sucked into the tube. By increasing of the number of carbon atoms up to 960, the amount of hydrogen molecules inserted was increased to 48. Other hydrogen molecules built up exohedrally around the tube (see the left side of Fig. 1). The MM calculations for (5,5)armchair, (9,0)zigzag and (7,3)chiral nanotubes did not reveal significant differences in H$_2$ adsorption. According to Molecular Dynamics, MD, [10] calculations the complex of (5.5)armchair nanotube with 655 H$_2$ molecules is stable at 10 K for at least 2 ns but decomposes at 50 K. Interestingly, at 10 K the removal of the central nanotube led to the destruction of the concentric rings formed by H$_2$ molecules.

A MM study of the nanotubes bundle consisting of 7 nanotubes and 655 hydrogen molecules have been carried out showing the high aptitude of hydrogen molecules for sucking inside nanotubes. The structure of the complex after minimization procedure is presented in Fig. 2. 84 H$_2$ molecules are situated only inside the nanotubes while the rest stays outside the bundle. MD simulations at different temperatures revealed that the thermal stability of the bundle is much higher than that of the ordinary nanotubes. The structure of the bundle surrounded by the hydrogen molecules during the simulation at 10 K is shown in Fig. 3. The higher temperature, the lower amount of H$_2$ molecules remains around the bundle. At 300 K only hydrogen molecules inside each nanotube of the bundle remain.

References
9. G. Dolgonos, H. Dodziuk, poster on the 32\textsuperscript{nd} Course “Strength from Weakness: Structural Consequences of Weak Interactions in Molecules, Supermolecules and Crystals”, Erice, Italy, 23 May - 3 June 2001.

Fig. 1. Two projections of the minimized structure of the supramolecular assembly consisting of armchair (5,5)nanotube of 220 carbon atoms and 285 hydrogen molecules.

Fig. 2. The nanotube bundle with 665 hydrogen molecules after minimization.

Fig. 3. The nanotube bundle with 665 hydrogen molecules after 100 ps at 10 K.
Structure and Photo-Activity Relationship of 12 Isomeric Methyl Benz[a]anthracenes

Shiming Dong, Anthony Moncrief, Huey-Min Hwang, Jerzy Leszczynski, and Hongtao Yu

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Polycyclic Aromatic Hydrocarbons (PAHs) are a class of environmental carcinogens. They are generally more toxic in combination with light. Therefore, studies were conducted on their ability to cause DNA cleavage in combination of UVA light. The PAHs used in study were: benz[a]anthracene (BA), the twelve mono methyl substituted BA derivatives, and 7, 12-dimethylbenz[a]anthracene (DMBA). These fourteen compounds have been categorized according to their respective DNA single strand photo-cleavage efficiency into three different categories: 1) Strong DNA cleavers (4-MBA, 5-MBA, 6-MBA, 8-MBA, 9-MBA, 10-MBA, BA), 2) Medium DNA cleavers (1-MBA, 2-MBA, 3-MBA, 11-MBA), and 3) Weak DNA cleavers (7-MBA, 12-MBA, and DMBA). Photo-cleavage efficiency in each MBA is shown to be proportional to the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) indicating that the DNA cleavage is related to its excited state properties. The photo-cleavage efficiency can be greatly reduced by methyl substitution at the 7 and/or 12 positions of BA, in which the UVA light induced photo-degradation is greatly enhanced, yielding products that are much less efficient in causing DNA cleavage. Photo-degradation of MBAs other than 7-MBA, 12-MBA, or DMBA yield photo-oxidation products that are relatively stable under light and are stronger DNA photo-cleavers than the original MBAs themselves. This is demonstrated by 5-MBA and BA, whose photo-oxidation products are 5-MBA-7, 12-dione and BA-7,12-dione, respectively. The 7,12-dione is largely responsible for the higher efficiency of DNA photo-cleavage by MBAs with methyl substitution at positions other than 7 or 12. Light-induced DNA single strand cleavage efficiency for several MBAs parallels the light-induced toxicity observed by other research groups, suggesting that light-induced DNA cleavage of MBAs be the source for photo-toxicity. Since some poly-aromatic hydrogen’s (PAHs) are widely used in various ways (such as commercial creams, ointments, or coal tar) persons who come into contact with PAHs may be subject to great health risks when exposed to light.
Intermolecular Electrical Response: A Deepening Insight for Expanded Applications

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That molecules respond to electrical environments is a basic part of chemical science. In the last decade, ab initio calculations of response properties have contributed substantially to our conceptual understanding and to our quantitative knowledge of molecular response to electrical environments. A specific kind of environmental change is that of intermolecular interaction, and with it, comes an electrical response that is important to determine. This can be considered from both the standpoints of interaction energetics and of property changes, and it can be approached via ab initio calculations and modeling. One objective is to devise models whereby measurable property changes can serve as probes of behavior associated with intermolecular interaction. The responses can be examined with finer and finer levels of detail, with each step opening up different applications problems from small cluster spectroscopy to polymer nonlinear optical response. Key objectives remain, especially in connecting certain analytical results with ab initio calculations—worthy objectives given the inherent transferability of electrical response properties and the ease of intermolecular electrical analysis.
Molecular Mechanics, Quantum Mechanics, Potentiometric and Conductometric Studies on the Complexes of Some Transition Metals with 5-Azorhodanine Derivatives

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The geometry of bivalent metal ions (Cu²⁺, Ni²⁺, Co²⁺, Mn²⁺) complexes with 5-azorhodanine derivatives was optimized at the level of molecular mechanics. Two stoichiometric ratios of metal to ligand (i.e., 1:1 and 1:2) were investigated. Tetra-coordinate and hexa-coordinate of each stoichiometric ratios have been studied. Effect of substitution in the ligand on the geometry of the complexes was discussed in the light of electron donation-accepting properties of these substituants. The influence of the nuclear effective charge of the central metal ions on the metal-ligand (M-L) bonding was discussed and the effect of the number of ligands on the M-L bond length was also discussed in the light of the experimental results. The binding energies of the different metal complexes were computed using extended Huckel method. The effect of substituants in ligand, metal type and stoichiometry of the complexes on the complex binding energies were discussed.

Stability constant of bivalent (Mn²⁺, Co²⁺, Ni²⁺ and Cu²⁺) metal ions with 5-azorhodanine derivatives have been determined potentiometrically in 0.1 M KCl and 50% (v/v) ethanol-water mixture. The order of the stability constants of the formed complexes was found to be Mn²⁺ < Co²⁺ < Ni²⁺ < Cu²⁺. The influence of substituents on the stability of the complexes was examined on the basis of electron repelling property of the substituent. The effect of temperature on the stability of the complexes formed was studied and the corresponding thermodynamic parameters (ΔG, ΔH and ΔS) were derived and discussed. The stoichiometries of these complexes were determined conductometrically and indicated the formation of 1:1 and 1:2 (metal:ligand) complexes
Density Functional Studies of Catalytic Alkane Dehydrogenation by Anthrophos Iridium Complex

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Thermostable homogeneous catalysts are important in the direct and selective conversion of saturated hydrocarbons to more useful, functionalized organic compounds. Because the dehydrogenation reaction from alkanes to alkenes is not only highly endothermic, but also symmetry forbidden, harsh reaction conditions, such as UV irradiation and high temperature, or special reagents such as a sacrificial hydrogen acceptor are usually needed in order to drive the reaction. Although first discovered in 1970s, it is only recently that pincer-like complexes have shown high thermostability and efficiency as catalysts for alkane dehydrogenation. However, the mechanism is not clearly understood. Both experimental and theoretical studies have suggested that the dehydrogenation can proceed by either transfer reaction or acceptorless reaction. The transfer mechanism uses a sacrificial hydrogen acceptor to make the whole process thermodynamically favorable and the oxidation state of metal center changes between Ir(III) and Ir(I), while the lowest energy acceptorless mechanism utilizes no sacrificial hydrogen acceptor and the oxidation state changes between Ir(III) and Ir(V). Jensen further proposed a third mechanism that the pincer complex might reductively eliminate the dihydride first before catalyzing the C-H activation. Krogh-Jespersen et. al also acknowledged that at the high reaction temperature, entropy could make important contribution to the reaction energetics.

Haenel and coworkers recent reported a highly efficient and stable pincer-like complex, anthrophos iridium dihydride complex. In this study, we will examine the possible pathways for the catalytic alkane dehydrogenation reaction by anthrophos iridium using density functional methods, including B3LYP and BP86. Factors such as energy barriers, entropy contributions, and free energy changes at various temperatures will be examined. These results will be compared with studies on pincer iridium complex and CpIr complex.

References

Jensen, C.M. Chem. Comm. 1999 2443
Effects of Local Movements of Charged Surface Residues on the Kinetics of Protein Dimerization Probed by Brownian Dynamics Simulations

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INTRODUCTION

Interest has focused for some time on the roles of charged amino acid residue R-groups on the surfaces of proteins in affecting recognition processes, but as yet no coherent code for their function has been established.1 Electrostatic interactions between charged groups on the surface of a protein and other protein surfaces or ligands are an obvious target for studies of recognition, as long-range electrostatic interactions are among the longest-ranged molecular forces recognized.2 A number of studies have been carried out in which the charged amino acids residing at the protein surface are catalogued and inferences about their function derived from structural and functional data,3 and individual charged amino acid residues have been mutated to uncharged and oppositely charged species, both singly and in groups, in experimental and computational studies;4,5 while somewhat quantitative explanations have been derived for the functions of individual charged residues in ligand recognition in these and other studies, no comprehensive set of rules has thus far appeared.

The study reported here continues previous work6,7 simulating a simple model protein system, the dimeric hemoglobin from the ark clam Scapharca inaequivalvis, in which individual charged residues were changed from their native-charge states to amino acids of neutral or opposite charge, and the effect of the change on the association rate coefficient for the dimerization reaction was calculated using Brownian dynamics simulations. The previous studies indicated that the individual loss of a charged residue changed the association rate coefficient by 0 – 60%, with most changes having little or no effect (0 – 10%) on the rate coefficient, likely because the affected residues lie distant from the interacting portions of the subunits in the most commonly used reorientation configuration pathways.7 The work described here examines the sensitivity of the association rate coefficient to the location of each charged residue, under the hypothesis that a significant change in the rate coefficient corresponds to a key charged amino acid residue which interacts consistently with charged groups on the other subunit during the formation of nearly bound configurations.

The way in which each charged residue was moved to gauge the effect of the move on the association rate coefficient was through a system of paired complementary mutations, in which each surface residue nearest to the residue of interest was converted to a species of that residue’s charge, while the residue of interest was converted to the charge state of the nearby residue. For example, the positive charge of Lys23 was moved closer to the binding face of the subunit by doubly mutating Lys23 to threonine (uncharged) and Gln78 (uncharged) to lysine (positively charged). It must be pointed out that the changes in position represent quantum movements of irregularly varying distance and direction, rather than continuous, isotropically disposed relocations, due to the requirement that the basic protein fold be preserved.
RESULTS AND DISCUSSION

The change observed in the association rate coefficient for mutants in which a charged surface residue has been moved one position away can be expressed in a couple of ways. The most significant expression of the sensitivity of the charged group to relocation is the average (root mean square) magnitude of change to the rate coefficient from the native (unmutated) charge pattern for all movements from that position, which are listed in order from most acceleratory mutations to most inhibitory mutations in the third column of the table, that is, from those positions in which the movement of the charge produced the greatest average increase in the rate coefficient to those producing the greatest average decrease. The other measure detailed in the table is in the fourth column, indicating how the average rate coefficient derived from relocations of a given charged residue differed from that corresponding to the simple removal of the charge at that position.

The average (root mean square) deviation of the relocated charges from the native charge pattern is relatively small, as might be expected. The native charge pattern on the hemoglobin monomer gives an association rate coefficient of $5.99 \pm 0.43 \times 10^5 \text{M}^{-1} \text{sec}^{-1}$, and thus the typical change to that rate coefficient by families of charge-movement mutations, on the order of $0.3 \times 10^5 \text{M}^{-1} \text{sec}^{-1}$, represents a change of approximately 5%. This small change is presumably due to the narrow dimerization kinetic pathways along which the subunits reorient themselves, as it is clear from previous work that few charged residues are sufficiently integral to the reorientation of the approaching subunits to affect the association rate coefficient strongly.\footnote{7}

Some charged residues stand out from the others in their respective effects on the rate coefficient for dimerization. For example, Arg104 shows the greatest decrease in rate coefficient when relocated to the position of a nearby residue. This effect likely arises from the unique position of Arg104 in the hemoglobin monomer: it is a lone positive charge at the edge of the site of heme insertion into the protein, and thus provides a significant charge-neutralizing function toward the propionate groups at the external edge of the heme group. Movement of Arg104 even a single amino acid residue distant reduces this charge neutralization, and the isolated negative charges of the heme propionates repel those of the companion subunit to a greater degree. This effect on the rate coefficient is also largely due to the fact that the heme groups in the subunits are at the edge of the binding face, such that the most productive, nearly bound configurations of the two subunits are strongly affected by this intensified electric field.

The group of residues giving a root-mean-square change to the rate coefficient greater than 0.325 (top of table: Lys29, Asp17, Lys105, Lys52, Lys96, and Asp64) appear to be near the edge of the binding face of each subunit, much as is Arg104. This may explain their large effects on the rate coefficient when moved, as the edge of each subunit is the most effective location for strongly interacting residues to assist in steering the binding faces toward one another, a fact observed in previous work.\footnote{7} Current work is directed toward identifying as many precise, atomic-level explanations for individual effects of these relocation mutations as possible, with the eventual goal of assisting in the development of an electrostatic recognition code for charged amino acid residues at the surfaces of interacting proteins.
Table. Sensitivity of individual charged residues to movement to nearest neighbors by double mutation. The number of nearby positions mutated to the charge of the given residue (first column), one at a time, while the charge of the given residue was converted to that of the nearby position, is given in the second column. The root mean square change in the association rate coefficient for that group of mutations is given in the third column, with the sign indicating whether the mutations predominantly increased or decreased the rate coefficient. The fourth column indicates the change in the average rate coefficient for the group from that for the null mutation (single mutation of a given residue to an uncharged species).

<table>
<thead>
<tr>
<th>Amino Acid Residue</th>
<th>Number of Positions Mutated</th>
<th>RMS Deviation in Rate Coefficient from Wild Type, (x 10^{-5}), M^{-1}sec^{-1}</th>
<th>Deviation of Average Rate Coefficient from Null Value (x 10^{-5}), M^{-1}sec^{-1}</th>
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<tr>
<td>Lys 29</td>
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REFERENCES
Ab initio Study of Irradiated Species of 1-Methyl Thymine and 1-Methyl Uracil

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One major consequence of ionizing radiation is its propensity to alter DNA which leads to the formation of radical nucleic acid species. The understanding of the properties of these radical species is vital to different aspects of DNA functioning, such as the mechanisms of replication and reparation subsequent to irradiation. Therefore, the investigation of different physical and chemical characteristics of radicals, which can be formed from DNA bases, is an important task for physical chemists.

To address this problem, we have performed a comprehensive investigation of the geometry and EPR parameters for 1-methylthymine (MT) and 1-methyluracil (MU) radicals. The geometries of local minima were optimized without symmetry restrictions by the gradient procedure at DFT and MP2 levels of theory and were verified by energy second derivative calculations. The standard 6-31G(d,p) and 6-311G(d,p) basis sets have been used.

We have found that the calculated equilibrium geometries of MT and MU are effectively planar, with spin densities $\rho$(N1) = .392 and $\rho$(C5) = .563. Computer hyperfine couplings are in agreement with the experimental couplings reported in [1]. However, both radicals possess the same type of structural nonrigidity as has been previously established for isolated DNA bases [2]. In the case of the corresponding DNA bases nonrigidity manifests itself by the presence of two low frequencies vibrations, which are associated with out of plane motion of the imide nitrogens. The same types of vibrations have been found in MTR and MUR.

For both species the EPR parameters such as spin densities and hyperfine coupling have been calculated and analyzed.

References
MP2 and DFT Studies of Geometrical Modifications Induced by Methyl Lesions in Guanine, Cytosine, and G-C Base Pairs

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The methylation of DNA is known to cause cancer. Methylation results from exposures to several chemicals found in the environment such as nitrosamines and diazoalkanes. It is well evidenced that DNA methylation alters the action of polymerases. The results of MP2 and DFT calculations are reported for methylation induced changes in geometries and interaction energies. In particular, we examined methylation at the guanine O⁶, N³, N⁷ and cytosine N³, O² sites. We calculated the relative stabilities for each lesion presented. These results will provide insight for future investigations aimed at understanding the mechanisms behind methylation induced mutagenesis.

Figure 1. Methylation of Cytosine at the O2 position
Comparative Study of the First Hyperpolarizabilities of Xylene Derivatives

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Ab initio calculations of the electronic contributions to the static first-order hyperpolarizabilities of 2,6-dinitro-3,5-dihalogen-p-xylenes will be presented. Values were obtained for fluorine, chlorine and bromine substituted xylenes. These compounds are known for presenting large quadrupole moments, and large first hyperpolarizability values for different cartesian components, their electronic distribution suffering the influence of inductive x resonance opposing effects by the halogens. Nitro is a standard electron acceptor group, and found in many molecules presenting nonlinear optical properties. This study compares the electron donating effects of F, Cl and Br, when coupled to nitro groups, in ortho position. All properties calculations were performed using 6-31G**++ (lacvp**++ for Br) at the Hartree-Fock level, after geometry optimization at the same level. Our results show how extremely sensitive the calculations are to small changes in structural parameters, and the unpredictability of the electronic response by the systems under study. There is a large discrepancy between our values and experimental ones found in the literature for similar systems. Some difference can be attributed to solvent effects and vibrational contributions, but not all of it. We will discuss the implications of comparing experimental values for the first-order hyperpolarizabilities with theoretical ones, which report only the electronic contributions to the static property.
Atmospheric Chemistry of Halogen Compounds:
Insights from Computational Chemistry

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Computational chemistry techniques have advanced to the stage where the applicability of such tools is playing an important role in assessing the impact of new halogen materials on the environment, as well as assessing the impact on global climate change. Previously, laboratory and field studies interfaced with atmospheric modeling studies provided the only means of assessing the impact of new materials on the environment. This talk will highlight a few examples of how computational chemistry studies are providing new insight into the characterization of new species, providing new insight into photochemistry in the atmosphere, as well as providing unprecedented mechanistic detail of the fate of chemical species once released into the atmosphere. New atmospheric chemistry directions will also be highlighted.
Insight into the Chemical Bond of Transition Metal Complexes

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Textbooks of Inorganic Chemistry present and discuss the chemical bonding in transition metal compounds in terms of qualitative heuristic models which have been suggested in the past when accurate quantum chemical calculations of the molecules were not possible. The lecture shows that modern charge and energy partitioning methods provide detailed insight into the mechanism of the bond formation. It is possible to derive an understanding of the metal-ligand bonds by analyzing the results of ab initio and DFT calculations which lead to qualitative models that are in agreement with the physical mechanism of the bond formation. This will be demonstrated for transition metal compounds with group-13 diyl ligands ER (E = B – Tl, R = Cp, Ph, Me). It is shown that the bonding interactions can be understood in terms of (a) donor-acceptor interactions in the framework of the Dewar-Chatt-Duncanson model and (b) electrostatic interactions between the local negative charge concentration of the ligand ER and the local positive charge of the metal fragment.

\[ \sigma \]

\[ \pi \]

\[ q(+)TM \]

\[ q(-) \]

\[ E \rightarrow R \]

\[ E \leftarrow R \]

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Rotational Mechanism and Thermochemical Properties of the Orthosilicic Acid, (Si(OH)$_4$) : A Theoretical Study

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A series of ab initio and density functional theory calculations have been carried out on various conformers of Si(OH)$_4$ to reinvestigate the geometry, vibrational spectra, and thermodynamical properties of model compounds for geochemically relevant silicate materials. Comparison of the HF, B3LYP, and MP2 (both frozen core and full core electron correlation) methods has been made with various basis sets. It has been shown that the D$_{2d}$ and C$_s$ conformers are minima on the potential energy surface, in addition to the global minimum of S$_4$ conformation, with their relative stabilities in the order S$_4$ > C$_s$ > D$_{2d}$. We notice that the selection of appropriate basis sets has significant influence on locating the C$_s$ and D$_{2d}$ geometries as minima. Thermodynamic parameters are calculated, at the G3 level of theory using the B3LYP/6-311++G(d,p) geometry and frequencies, based on the new conformers at different temperatures. A good agreement between theoretical and experimental results (at 1600K) has been found. Rotational transition structures between the conformers are computed at different levels of theory with a variety of basis sets and a comparison is made.
Effect of Coordinated Water on the Mechanism of Hydrolysis of Silicon Dioxide in Gas Phase: A First Principles Study

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As the most abundant substance on earth, silicates have been found to influence a multitude of processes of general and industrial importance such as complexation with nucleosides, catalysis of polymerization reactions, synthesis of organic molecules from inorganic matter, formation of silicon oxide thin films for microelectronic devices, etc.\textsuperscript{1,2} Such activity of silica is believed to be dependent on the number of available hydrogens and hydroxyls of the Si-OH surface groups. However, the mechanistic nature of surface hydrolysis of silicate from the gas phase is largely ambiguous. Therefore, a series of ab initio and density functional theory calculations have been carried out on the mechanism of hydrolysis of silicon dioxide to orthosilicic acid, Si(OH)\textsubscript{4}. The effect of coordination to the silicon is studied with one and two water molecules. It is shown that second water coordination reduces the reaction barrier by ~50\% with an overall low barrier reaction steps (Figure 1). The rate determining step is the formation of SiO(OH)\textsubscript{2}(H\textsubscript{2}O).\textsuperscript{6} Comparison of the B3LYP and MP2 (frozen core electron correlation) methods has been made with 6-311++G(d,p) basis sets. Since it is ideal to have basis sets converging to the basis set limit, we have chosen the so called hierarchical basis sets of cc-pVTZ usually used in correlated level calculations for such capability.\textsuperscript{3} The transition structures were located using the Synchronous Transit-Guided Quasi-Newton (STQN) Method, developed by Schlegel and coworkers.\textsuperscript{4} Thus the mechanistic studies based on ab initio MO theory predict that hydration and hydrolysis of silicon dioxide in the gas phase to orthosilicic acid is controlled by the coordinated water molecule at the silicon. This is in contrast to the hydration of carbon dioxide where the coordination at the carbon is less feasible.
Figure 1. Reaction energies (kcal/mol) at B3LYP/6-311++G(d,p), MP2(FC)/6-311++G(d,p), and MP2(FC)/cc-pVTZ levels respectively (from top to bottom).

References

Ab Initio MO Study of ArₙH⁺ (n=1,7) Clusters

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Geometries, vibrational frequencies, and dissociation energies of protonated argon clusters obtained at the MP2 and CCSD(T) levels of theory using high angular momentum basis functions of 6-311++G(3df,3pd) are reported. A full core electron correlation was taken into account. The geometries of the ArₙH⁺ (n>3) based in the present study are very different from those reported in literature. The bonding nature and an interaction energy decomposition are discussed.
Tautomeric Properties of Guanine. 
Chemical and Biological Overview

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Computational Center for Molecular Structure and Interactions, Department of Chemistry, 
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This work addresses the significance of thermodynamic and kinetic parameters of the intramolecular proton transfer in guanine and its monohydrated complexes from the chemical and biological viewpoints. For this purposes the corresponding free energies, equilibrium and rate constants have been calculated and analyzed at different levels of Möller-Plesset perturbation theory. We have found that the time to reach 90% of equilibrium concentration starting from 1 M of canonic or ‘rare’ form of guanine could be estimated to be approximately 73 hours. Thus we concluded that both canonical and ‘rare’ forms of guanine are kinetically unstable species. The rate of tautomeric transition is accelerated drastically if water molecule is placed in the thermodynamically most likely position of the canonic form of guanine. The almost three-fold decrease of proton transfer barrier and the preference in the stabilization of canonic form lead to the establishment of the equilibrium concentrations instantly.

The results revealed above have been used for a qualitative discussion of some aspects of DNA synthesis accompanied with spontaneous point mutations. In particular, the role of tautomeric proton transfer process resulted in the transformation of guanine into its ‘rare’ form has been discussed with respect to spontaneous GC → AT transition. Two possible biological consequences follow from our study. Obtained data do not contradict M. D. Topal and J. R. Fresco’s mechanism of appearance of spontaneous point mutations through the establishment of two equilibrium steps during the synthesis of DNA. Nevertheless, they also allow to consider of completely different mechanism of GC → AT spontaneous point transitions through the pathway that excludes the equilibrium steps.
Possible Nature of Mutagenesis Under Activity of Free Radicals

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It is well known, that the basic contribution to damages of DNA under activity of ionizing radiation is made by free radicals formed as a result of radiolysis of water. Mainly these are the active forms of oxygen [1]. The basic part of spontaneous mutagenesis also occurs under activity of free radicals appearing in the process of metabolysis [2]. As well as at the activity of ionizing radiation the basic damaging agents are the active forms of oxygen [2]. Therefore the chemical nature of spontaneous damages of DNA and damages caused by ionizing radiation in a large extend is identical. Also they are repaired in the same ways [3]. Hence, their natures of mutagenesis are the same.

The oxidizing modification of DNA results in tearing up of sugar-phosphate connections, damages of the bases, to damages of desoxyribose and occurrence of new covalent bonds [1,2]. There are some tens of stable types of the modified bases [1,2]. As a rule, the modifications of the bases occur in the position ? 5 -? 6 in pyrimidines and ? 8 in purines. Besides the modification of guanine in the position ? 2 and adenine in the position ? 6 was observed [4,5].

The middle stage of formation of the stable modified bases is the formation of short-living free radicals and radical - ions of the DNA bases [6]. The study of short-living free radicals of the bases, nucleosides and nucleotides in water solution and single crystals by the EPR method enabled to make the following deduction. In comparison with the state in the initial molecule the unpaired electron in a radical does the major action on ionization constant and tautomerizing of a radical. This action can cause dissociation and tautomerizing in another position [6]. It was shown, that the given deduction is valid also for the native DNA [6].

Sometimes in strongly exothermal reactions the energy of chemical reaction remains in the form of electron energy, so one of the products of reaction is formed in the electron-excited state. It was shown, that taking an electron from an anion-radical of polycyclic aromatic hydrocarbons or the addition of an electron to a cation - radical often results in formation of a neutral substrate in the electron-excited state. The transferring of an electron can be induced by oxidizing agents, reducers or under activity of an electrical current. Other vivid examples are decomposing peroxides and oxygen which is in an excited state (singlet oxygen had been properly investigated) [7].

If deexcitation of electronic-vibration quantum of energy occurs from the singlet level of energy, the most probable process is the radiation of energy. For example, the singlet states of oxygen correspond to energies 38 kcal / mol and 76 kcal / mol and the red luminescence (chemiluminescence) is observed.

If deexcitation occurs from the triplet level of energy, the most probable process is the non-radiative relaxation of energy. Let's consider a pair of the bases in the chain of DNA. Let as a result of reaction with the active forms of oxygen one of the bases turned into a short-living modified radical or a radical-ion. Let as a result of taking an electron from an anion-radical of the basis of DNA the modified basis of DNA, which is in an electronic-vibration excited state was formed. Let deexcitation occurs from the triplet level of energy. Then there will be the processes described in [8,9] in the result of which there will be a change of the tautomeric form such, which affects the content of hydrogen participating in pairing of the bases.
If the DNA damages are such ones the DNA chain has become twisted and H-bonds are broken the stable position will be all new ones of the hydrogen atoms.

If the H-bonds are remain than, perhaps, only one new tautomeric form will be stable. This is when in the pair G-C the atom $H'_4$ of cytosine forms a valence bond with guanine, and $H_1$ of guanine forms a valence bond with cytosine. Similarly in the pair A-T the configuration, when $H'_6$ of adenine forms a valence bond with thymine, and $H_3$ of thymine forms a valence bond with adenine will be stable [10]. This statement is correct, if the deductions [10], obtained for canonical pairs G-C, are valid also for the modified bases. The change of tautomeric state occurs at both of paired bases, i.e. both chains of DNA are damaged. Apparently, only in a very small part of the modified bases there is a change a tautomeric state, influencing the character of pairing, of the bases.

The modified bases are removed by the same systems of reparation, as pyrimidine dimers. Therefore deductions made for mechanisms of formation of mutations of replacement of the bases at SOS-reparation of DNA, containing thymine dimers [9], in basic will be valid both for a spontaneous mutagenesis as well as for the mutagenesis under activity of ionizing radiation. Therefore we can offer a model, based on the following hypotheses: 1. Not all modified under activity of the active forms of oxygen and other free radicals bases result in mutations, but only those in which there was such a change of tautomeric state, which can influence the character of pairing of the bases. 2. The mutations occur as a result of an induction of SOS-system at replication and reparation. The repressing of activity of $3\rightarrow 5'$ – exonucleases in comparison with DNA-polymerases is expressed, in particular, that the check of the tautomeric state of the bases of template is weakened. 3. Only the bases which are in the canonical tautomeric forms and capable to form hydrogen bonds with the bases of matrix are built in. 4. Another source of mutations can be the change of orientation of the bases with respect to the sugarphosphate stroma. Such changes of orientation can take place because of the damages of sugarphosphate stroma itself or infringement of hydrogen bonds, stabilizing the location of the bases with respect to the sugarphosphate stroma.

The list of the literature

A Novel Motif of Cytosine Tetrad: A Theoretical Study

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As an extension of our previous studies on DNA base tetrads, the molecular structures and the stabilities of the cytosine tetrad have been investigated using the \textit{ab initio} HF method and the density functional theory. We report here the first quantum chemical prediction of a new motif of the C-tetrad, its stabilization energy, and its electrostatic potential characteristics. The H-bonding pattern involved in this tetrad conformer seems to be consistent with the experimental NMR spectrum.

The tetrad structure adopts a planar form with atoms’ deviation from the plane less than 0.001 Å. Instead of the large cavity conformer, the present study has predicted the small cavity pattern, in which the four non hydrogen-bonded amino protons point to the center of the tetrad. Both the amino protons interact weakly with the N1 atom of the neighboring base. The atomic distance between N1 and H(N4) predicted at the DFT level are 2.70 Å for the hydrogen-bonded proton and 2.75 Å for the non hydrogen-bonded one. In the NMR measurement, the proton chemical shifts of 6.62 ppm and 5.83 ppm, respectively, were observed for the amino protons. These large upfield shifts was suggested to occur due to the protons stack over the adjacent G tetrad. However, the influence of the neighboring N1 presented in our small cavity model seems to play a more important role in the origin of these large shifts. The atomic distance between the non hydrogen-bonded amino protons from the opposite cytosine bases is calculated to be 4.73 Å. This results in formation of a cavity similar to the one observed for the G-tetrad in the presence of a cation. The small cavity size predicted in this novel conformer implies that its non hydrogen-bonded amino protons are ready to stack over the O6 atoms of the successive guanine tetrads, if there is no intercalated cation. The stabilization energy of the C-tetrad is predicted to be 56.41 kcal/mol at the DFT level. A main factor for this very lager stabilization energy of the C-tetrad can be revealed by the examination of its electrostatic potential map. It indicates that there is no electrostatic repulsion in the center of the cavity.

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A novel motif of C-tetrad predicted at the DFT level and its electrostatic potential map.
Characterization of Chemical Reactions through Classical Concepts and DFT Descriptors

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In this paper we point out that classical concepts of reactivity in connection with Density Functional Theory (DFT) descriptors are adequate and powerful tools for characterizing chemical reactions. Within the framework of the Hammond postulate and Marcus equation we introduce the principle of maximum hardness to check the consistency between energetic and electronic properties. Few illustrative examples of representative systems undergoing different kinds of chemical reactions confirm the validity of this approach.

Understanding chemical reactivity allows one to predict the reaction mechanism and to determine how the activation energy depends on specific properties of reactants and products. DFT, through the definition of few interesting global and local reactivity properties, is well suited to describe the electronic reorganization that takes place during a chemical reaction. On the other hand, to characterize transition states there is a set of conceptual tools that give complementary insights on their structure and properties. These conceptual tools are: (a) the Hammond postulate that interrelates the position of the transition structure to the exothermicity of the reaction; (b) the Marcus equation that provides a simple expression for the activation energy in terms of the reaction energy and the structural properties of reactants and products; and (c) the Principle of Maximum Hardness that asserts that molecular systems at equilibrium tend to states of high hardness, therefore TS's are expected to present a minimum value of hardness. The connection between DFT and classical reactivity concepts is the subject of this work.

Within the conceptual frame of DFT a complete characterization of an \(N\)-particle wavefunction needs only \(N\) and the external potential \(\psi(r)\), the energy of the system may be expressed as a function of \(N\) and a functional of \(\psi(r)\), so \(E[\rho(\psi(r))] = E[N, \psi(r)]\). When a reaction move forward along the reaction coordinate, a redistribution of the ground-state electron density occurs, the resulting change of the energy can be rationalized in terms of the response of the system when changing \(N\) and \(\psi(r)\) and can be characterized through the derivatives of the energy with respect to these variables, these derivatives define global and local chemical reactivity descriptors.

The response of the system when \(N\) is varied for a fixed \(\psi(r)\) is measured by the chemical potential \((\mu)\) and the hardness \((\eta)\) while local properties, such as the Fukui function, measure the response of the system for changing the external potential at constant \(N\). To understand the behavior of the system for changing \(\psi(r)\) at constant \(N\), we will use the polarizability \((\alpha)\), another global property of the system. In numerical applications, \(\mu\) and \(\eta\) are calculated through the following approximate equations based upon the finite difference approximation and the Koopmans' theorem:
\[ \mu \approx -\frac{1}{2} (I + A) \approx \frac{1}{2} (\varepsilon_L + \varepsilon_H) \]

\[ \eta \approx \frac{1}{2} (I - A) \approx \frac{1}{2} (\varepsilon_L - \varepsilon_H). \]

\( I \) is the ionization potential, \( A \) is the electron affinity, \( \varepsilon_H \) and \( \varepsilon_L \) are the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively.

On the other hand, the energy of the TS is determined through the Marcus equation:

\[ \Delta E^\# = \frac{1}{4} K_E + \frac{1}{2} \Delta E^o + \left(\frac{\Delta E^o}{4K_E}\right)^2, \]

that provides the necessary framework for a quantitative analytic representation of the Hammond postulate.

Applications.

Rotational Isomerization. We present results for the trans \( \leftrightarrow \) cis isomerization reaction in the HXNY (X,Y=O,S) series of molecules. We have determined the \textit{ab initio} Hartree Fock and DFT profiles of energy, chemical potential, hardness and polarizability along the torsional angle and found the validity of the principles of maximum hardness (PMH) and minimum polarizability (PMP) in these rotational systems. The energy minimum is associated with a maximum of hardness and a minimum of polarizability whereas the TS is associated with a hardness minimum and a maximum of polarizability. It is shown that in these cases the maximum hardness and minimum polarizability condition nicely complement the minimum energy criterion for molecular stability.

Intramolecular Rearrangement Reactions. Hartree-Fock and DFT results for a number of systems undergoing intramolecular rearrangement are presented. Here again the profiles of the energy and electronic global properties, exhibit the trends that are expected from the PMH and PMP, in most cases the TS has been found to be softer and more polarizable than the reference stable conformations.

Double Proton Transfer in \((\text{HCXYH})_2\) (X,Y=O,S). We present results for double proton transfer (2PT) reactions in bimolecular complexes formed by combinations of molecules of the type CHX-YH (X,Y=O,S). Characterization of various properties of the transition states allows one to identify the specific interactions stabilizing the complexes and helps determine the physical nature of the energy barrier for the simultaneous transfer of two protons. The profiles of \( \eta \) and \( \alpha \) indicate the simultaneous validity of the principles of maximum hardness and minimum polarizability. Transition state structures are therefore characterized through a maximum value of energy and polarizability and a minimum value of hardness, as required by the PMH and PMP.

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References.
Computation of Ring Strain in Azetidine and Phosphetane

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The strain energies for azetidine (Figure I.) and phosphetane (Figure II.) are determined within the isodesmic, homodesmotic and hyperhomodesmotic models. Optimum equilibrium geometries, harmonic vibrational frequencies, and corresponding electronic energies are computed for all pertinent molecular systems using SCF theory, second-order perturbation theory, and density functional theory (DFT). The DFT functional employed is Becke- three parameter hybrid functional using the LYP correlation functional. Two basis sets, both of triple-zeta quality on valence electrons, are employed: 6-311G(d,p) and 6-311++G(2df,2pd). Finally, the strain energies of azetidine and phosphetane are compared to those of cyclopropane, cyclobutane, 1,2-oxazetidine (Figure III.), and 1,3-oxazetidine (Figure IV.). We gratefully acknowledge support from NSF EPSCoR (EPS-9874669).
Exchange and Correlation in Density Functional Theory

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The major success for Density Functional Theory in computational Chemistry is the introduction of LOCAL exchange and correlation functionals. In this talk we shall discuss exchange, left-right correlation and dynamic correlation for electrons. In particular we shall, with reasons, argue that

1. All correlation in atoms is dynamic
2. Exchange functionals should reproduce Hartree-Fock energies of atoms
3. We cannot find a functional which returns CASSCF energies of atoms
4. Exchange functionals should not reproduce Hartree-Fock energies of molecules
5. Exchange functionals introduce left-right correlation
6. The binding energy of a molecule has a significant contribution from both left-right correlation and dynamic correlation
7. Atomic data can be used to determine exchange functionals and correlation functionals
8. Hybrid functionals deteriorate as a molecule is distorted

We shall introduce new exchange functionals and new correlation functionals.
We shall argue against (i) hybrid functionals, (ii) functionals which return Hartree-Fock energies for molecules, (iii) functionals which return electron gas properties for constant densities.
Shifting Balance between Computation and Experiment

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Although the talk will concentrate on the development of the past ten years and focus on molecular structure research, I will place the topic in a broader perspective. At least from Gay Lussac there has been a conscious effort by distinguished chemists to calculate chemical quantities. In the early 1950s, John Pople charted a development program according to which computations of gradually increasing sophistication were applied to a variety of chemical problems during the ensuing decades. At first, the task was to merely augment experimental studies with computation if only to signal awareness of the emerging techniques. Later, computational work gained acceptance as being on a par with the experiment. By now there are problems of chemistry for which computational techniques may be used preferentially either for cost or reliability considerations or simply because no experimental approach is feasible or even possible. The mistrust of the early years toward computational results by many chemists has been replaced first by moderate curiosity and by now by ever broadening acceptance. John Pople put it still in modest terms when, in 1995, asked about the ideal relationship between experimental and computational work: “I view computations as a technique which any chemist can use, including experimentalists. These calculations should augment the experimental work.” [I. Hargittai, Candid Science: Conversations with Famous Chemists. Imperial College Press, London, 2000, pp. 178-189.]

The presentation will focus on the experience in the Structural Chemistry Research Group in Budapest over the past decade. Two areas of research will be highlighted, viz., the formation and structural consequences of intramolecular hydrogen bonding and the rich variety of metal halide molecular structures. In both areas, experimental and computational work has been carried out in a concerted and most fruitful way.

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Quantum Monte Carlo Studies of the Ozone Molecule

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The electronic structure of the ozone molecule has long been considered challenging for traditional electronic structure methods. Particularly interesting quantities, both theoretically and experimentally, are the bond dissociation energy, the total atomization energy, and energies of low-lying electronic excited states. This study applies the QMC method to ozone, in order to estimate its atomization and bond dissociation energies. We make comparisons to experimental and other theoretical estimates of these quantities.
X-Ray Crystallography: A History of Ideas

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In this account it is my aim to write about some of the ideas which have made possible the science of X-ray crystallography as we know it today. X-Ray crystallography, since its birth in 1912, has undergone an explosive development. This rapid growth is no doubt due in part to the fact that this science lies at the intersection of many scientific disciplines: Chemistry, Physics, Mathematics, Materials Science, Biology, and the other life sciences. Not only have these sciences benefited from the rapid development of crystallography in the twentieth century but the phenomenal growth of the science of X-ray crystallography in turn was made possible through its interactions with these diverse scientific disciplines.

A remarkable feature of the ideas and discoveries which made possible the development of X-ray crystallography in the twentieth century is that they were, in large part, conceived many years, in some cases centuries, before the birth of X-ray crystallography itself. Thus these ideas, at the time they were formulated, had no obvious relationship to crystallography; they had been conceived instead for some other purpose having no apparent connection to our science. What were these ideas and what were their connections with X-ray Crystallography?

My intention in writing the first half of this account is to give some of the answers to these questions and to stress that, in large part, these ideas and discoveries could not, or would not, have been made had not the previous ones been made first.

The second half of this article is, on the other hand, dedicated to those ideas having a direct and obvious relationship to X-ray crystallography. They were conceived with the specific purpose of solving some problem in X-ray crystallography itself.