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**Report Title**

4.6 Terahertz Science & Technology: Stilbene & Its Derivatives for Multi-State Spectral Sensing


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We study photo-induced transitions of stilbene and its derivatives and the change of vibrational spectra as a result of these transitions. All derivatives have vibrational frequencies in the THz region with a large difference in frequencies between two isomers. TMS-DNA structure, (TMS-TGCGCA)2, is optimized. The oscillator strength against frequency characteristics for both cis-TMS capping with DNA and trans-TMS capping with DNA structures is determined.


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## Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

### (a) Papers published in peer-reviewed journals (N/A for none)

| Received | | Paper |
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| 2012/02/24 1 | 4 | X. Li, T. Globus, B.Gelmont, L.C.Salay, A.Bykhovski. Terahertz Absorption of DNA Decamer Duplex, Journal of Physical Chemistry A, (10 2008): 0. doi: |
| 2012/02/24 1 | 8 | Tatiana R. Globus , Michael L. Norton , Maryna I. Lvovska, Derek A. Gregg, Tatyana B. Khromova, Boris L. Gelmont. Reliability Analysis of THz Characterization of Modified and Unmodified Vector Sequences, IEEE Sensors Journal, (03 2010): 0. doi: |
| 2012/02/24 1 | 11 | Ramakrishnan Parthasarathy, Tatiana Globus, Alexei Bykhovski, Nathan Swami, Boris Gelmont. Terahertz (THz) Electromagnetic Field Enhancement in Periodic Subwavelength Structures, IEEE Sensors Journal, (06 2008): 0. doi: 10.1109/JSEN.2008.923222 |
| 2012/02/23 1 | 3 | Boris Gelmont, Tatiana Globus. Edge effects in perfectly conducting periodic subwavelength structures, IEEE Transaction on Nanotechnology, (01 2011): 83. doi: |
| 2012/02/23 1 | 6 | R. Parthasarathy, T. Globus, B. Gelmont. Edge effects in propagation of terahertz radiation in subwavelength periodic structures, SEMICONDUCTORS , (08 2008): 0. doi: |
| 2012/02/23 1 | 2 | Yikan Chen, Zhen Xie, Ying Luo, Boris Gelmont, James Jensen. Stilbene and Its Derivatives for Multi-State Spectral Sensing, IEEE Transactions on Nanotechnology, (05 2010): 558. doi: |
| 2012/02/23 1 | 1 | Alexei Bykhovski , Boris Gelmont. The Influence of Environment on Terahertz Spectra of Biological Molecules, Journal of Physical Chemistry B, (10 2010): 12349. doi: |

**TOTAL: 7**

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## (c) Presentations

1.B. Gelmont THz Science & Tehcnology: Stilbene and Its Derivatives for Multi-State Spectral Sensing, EDSDS Workshop, Raleigh, NC, 3/18-20/2009
2.Boris Gelmont,"THz Science & Tehcnology: Stilbene and Its Derivatives for Multi-State Spectral Sensing",MURI Meeting,Washington,DC, July 13-14,2011
3.Boris Gelmont, Tatiana R. Globus, "Edge effects in perfectly conducting periodic subwavelength structures", 2009 Nanoelectronic Devices for Defense & Security (NANO-DDS), Fort Lauderdale ,FL, September 2009.
4.Boris Gelmont, Yikan Chen, Zhen Xie, Ying Luo, James Jensen, "Stilbene and Its Derivatives for Multi-State Spectral Sensing", 2009 Nanoelectronic Devices for Defense & Security (NANO-DDS) , Fort Lauderdale ,FL, September 2009.
5. Alexei Bykhovski, Boris Gelmont, "The Influence of Environment on THz Absorption of Biological Threat Agents" , ISSSR 2010 Springfield, Missouri ,June 21 - 24, 2010.
6.Tatiana Globus, Boris Gelmont, C. Neal Stewart, Reginal J. Millwood, Michael L. Norton ,"Terahertz Spectroscopic Signature From Short Artificial DNA Molecules with Well Controlled Structure", ISSSR 2010, Springfield, Missouri ,June 21 - 24, 2010.

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## Awards

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|---|---|
| **FTE Equivalent:** | |
| **Total Number:** | |

### Names of Post Doctorates

| NAME | PERCENT_SUPPORTED |
|---|---|
| **FTE Equivalent:** | |
| **Total Number:** | |

### Names of Faculty Supported

| NAME | PERCENT_SUPPORTED | National Academy Member |
|---|---|---|
| Boris Gelmont | 0.30 | No |
| Igor Sizov | 0.30 | |
| **FTE Equivalent:** | **0.60** | |
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### Names of Under Graduate students supported

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| | |
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| Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale): ..... | 0.00 |
| Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering: ..... | 0.00 |
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### Names of Personnel receiving masters degrees

| NAME |
| --- |
| Zhen Xie |
| Yikan Chen |
| **Total Number:** 2 |

## Names of personnel receiving PHDs

| NAME |
| --- |
| R. Parthasarathy |
| **Total Number:** 1 |

## Names of other research staff

| NAME | PERCENT_SUPPORTED |
| --- | --- |
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| **Total Number:** | |

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## Inventions (DD882)

## Scientific Progress

This work is the part of a broad research on bio-molecular-based device concepts for enhanced sensing Terahertz (THz) frequency bio-signatures using Multi-Photon, Multi-Wavelength Processes within Bio-Molecular Architectures. Terahertz region in the vibrational spectra of a certain molecule reveals the intramolecular vibrations between weakly bonded or non-bonded groups. Additional information can be acquired by photo-induced transitions between metastable states of the target agent. Research Goal is to provide important information regarding the general feasibility of multi-state spectral sensing. Different isomers of stilbene and its derivatives can be utilized in order to obtain the spectral “terahertz fingerprint” using multi-state spectral sensing technology. As the first step basic parameters of stilbene and its derivatives have been determined in order to prove the feasibility of detectors utilizing these molecules.

One of the most useful characteristics stilbene and its derivatives own is that they are able to form very stable bridged hairpins with DNA. TMS-DNA structure is one of the most stable one among various kinds of stilbene-DNA structures. As the next step 3,4,5-trimethoxystilbene carboxamidopropane (TMS) -DNA structure has beeen optimized.By performing normal mode analysis (NMA) over the optimized structure, it is possible to get the oscillator strength against frequency characteristics for both cis-TMS capping with DNA and trans-TMS capping with DNA structures.

## Technology Transfer


*Final Report*

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# THz Science & Technology: Stilbene and Its Derivatives for Multi-State Spectral Sensing

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***Abstract*—Terahertz region in the vibrational spectra of a certain molecule reveals the intramolecular vibrations between weakly bonded or non-bonded groups. Additional information can be acquired by photo-induced transitions between metastable states of the target agent. Different isomers of stilbene and its derivatives can be utolized in order to obtain the spectral "terahertz fingerprint" using multi-state spectral sensing technology. Also stilbene and its derivatives are able to form "capping" with DNA, making them very important covalent linker with DNA terminus to increase the fidelity of DNA duplexes as oligonucleotide hybridization probes. TMS-DNA structure is one of the most stable one among various kinds of stilbene-DNA structures.**

**We study photo-induced transitions of stilbene and its derivatives and the change of vibrational spectra as a result of these transitions. All derivatives have vibrational frequencies in the THz region with a large difference in frequencies between two isomers. TMS-DNA structure, $(TMS\text{-}TGCGCA)_2$, is optimized. the oscillator strength against frequency characteristics for both cis-TMS capping with DNA and trans-TMS capping with DNA structures is determined.**

***Keywords-stilbene, multi-state spectral sensing, TMS***

This work is the part of a broad research on bio-molecular-based device concepts for enhanced sensing Terahertz (THz) frequency bio-signatures using Multi-Photon, Multi-Wavelength Processes within Bio-Molecular Architectures.

**Research Goals:**

Terahertz region in the vibrational spectra of a certain molecule reveals the intramolecular vibrations between weakly bonded or non-bonded groups. Additional information can be acquired by photo-induced transitions between metastable states of the target agent. Research Goal is to provide important information regarding the general feasibility of multi-state spectral sensing. Different isomers of stilbene and its derivatives can be utilized in order to obtain the spectral "terahertz fingerprint" using multi-state spectral sensing technology. As the first step basic parameters of stilbene and its derivatives have to be determined in order to prove the feasibility of detectors utilizing these molecules.

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By performing normal mode analysis (NMA) over the optimized structure, it is possible to get the oscillator strength against frequency characteristics for both cis-TMS capping with DNA and trans-TMS capping with DNA structures.

## 1. INTRODUCTION

The submillimeter-wave frequency regime (i.e., ~ 0.1-10 THz) is predicted to be fairly rich with spectral features that are dependent on internal vibrations involving weakly bonded or non-bonded groups spread over large portions of the complex molecules. Since these vibrational modes are unique to a particular molecule, the THz region may allow the identification of unknown substances through a spectral 'terahertz fingerprint'. Previous research shows that THz sensing has the potential to be applied as general characterization of biological agents by detecting and identifying hidden dangerous biological materials through their transmission or reflectivity spectra. Experiments based on transmission features of Salmon DNA and Herring DNA give supportive data on that.

However, simple THz sensing technology cannot be widely used because the output power of available sources is limited. In addition the absolute absorption is relatively weak. To conquer this bottleneck, Multi-state Spectral Sensing technology is developed. Changes of the microscopic conformational structure of bio-molecules stimulated by external factors will affect changes in THz spectral signatures. Multi-state Spectral Sensing is the methods of incorporating biological elements with electronic architecture to achieve higher-level function and spectral data processing within a nanoscale and molecular-level architecture. It is able to expand the amount of available spectral signature information.

To obtain better control effects, suitable molecule system for Multi-state Spectral Sensing should be chosen. A good molecule system should contain two or more metastable states with different geometries, and these conformational states can be switched by external force, such as photo induced transitions and voltage induced transitions.

The impact of this research is that it will derive Terahertz (THz) spectral bio-signatures for organic molecules that are amenable to photo-induced metastable state conformations, define THz properties associated with both electronic and geometrical transformations of bio-molecules under the influence of coupling to other organic and inorganic systems and will establish an initial scientific foundation and design blueprint for an enhanced THz bio-signature sensing capability.

Different isomers of stilbene and its derivative 3,4,5-trimethoxystilbene carboxamidopropane (TMS) can be combined with DNA structure. Oligonucleotides are widely used as hybridization probes, primers, and biomedical agents. In common cases it is quite often for oligonucleotide hybridization probes to match their target sequence in a sea of competing sequences. High fidelity hybridization probes should bind their fully complementary target sequence precisely. This is crucial when single-nucleotide resolution is required, either because the expression of genes from closely related families of proteins is to be monitored or because single-nucleotide polymorphisms are to be detected by hybridization.

This target can be achieved without difficulty inside the duplex of DNA because one mismatch base pair will affect several pairs near them and the stability will fall significantly. However, this is not true for DNA terminals due to fraying and few neighboring base pairs affected. Even for some short oligonucleotides, a mismatch at the terminus results in the decrease of the UV-melting point by only a few degrees, and the free energy of binding by <1 kcal/mol, both for DNA and for RNA. Due to the low fidelity of the termini of duplexes, the usefulness of DNA is limited.

This problem can be solved by capping the termini with covalent linkers, such as stilbene and its derivatives. Stilbene-DNA is able to form very stable bridged hairpins. Letsinger et.al. [1] found that stilbene-carboxamides were better bridges for hairpins. Moreover, based on experiments focusing on the UV-melting point for different kinds of stilbene-carboxamides, the highest melting point is detected for 3,4,5-trimethoxystilbene carboxamide (TMS) [2].

Also TMS capping is important for the following 2 reasons [3]:

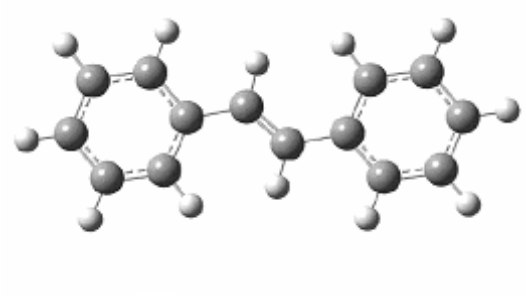
1.Many key biochemical processes contain the steps between DNA terminus and an external ligand. TMS-DNA binding system can be a good reference for research on these problems.

2. TMS-DNA capping provides a planar surface where π-stacking interactions can be studied more extensively than usual in folded bio-macromolecules.

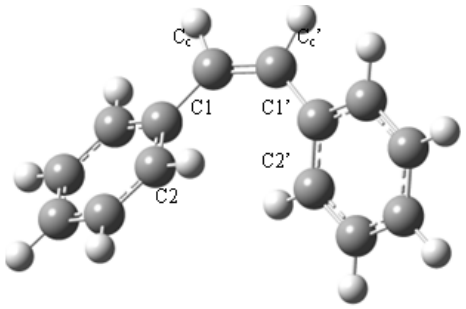
This work introduces the multi-state spectral sensing for terahertz technology and stilbene and its derivatives, then performs simulations and experiments on different conformations of isomers with the density functional theory in gas phase showing the potential energies curves and surfaces for both ground state and excited state of stilbene and one of its derivates TMS.

## 2. STILBENE AND ITS DERIVATIVES

Cis- and trans- stilbene are two isomers, shown in Fig. 1. In this type of isomers, two conformations result from the restricted rotation around the carbon-carbon double bond (C1-C1'). Compared with other molecules such as long chain structure, ring-contained structure in stilbene is more stable and these two isomers can be converted to each other under light excitation. Quantum yield of this isomerization can be tuned by the solvent, medium viscosity, and temperature. In addition, chemistry of stilbene allows for the creation of various functional derivatives.



trans-stilbene




cis-stilbene

Fig. 1 Structures of trans- and cis-stilbene

***A. Stilbene***

The infrared spectra of cis- and trans- stilbene are calculated with with the DFT using B3LYP/6-31G(d) function . The low-frequency part is shown in Fig. 2. It can be observed in Fig. 2 that strongest peaks of cis- and trans-stilbene located at 55 $cm^{-1}$ and 239 $cm^{-1}$ respectively are quite different. Cis-stilbene is dominating at higher-frequency region. Moreover, no vibrational modes are detected under 30 $cm^{-1}$. These are expected for various stilbene derivatives.

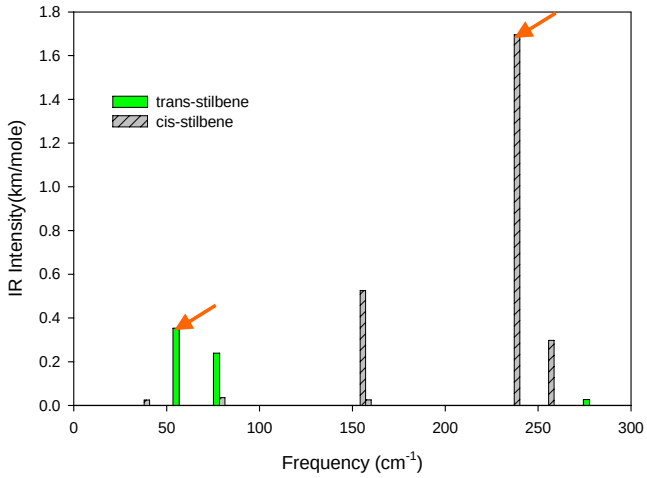



Fig. 2 Infrared spectra of stilbene

Six stilbene derivatives with different side groups or combination of side groups are studied with geometric structures shown in Figure 3. In (a), a nitro group is linked to one phenyl ring while in (b) it is replaced by a methoxy group. In trans-4-methoxy-4'-nitrostilbene, one methoxy group is added to one phenyl ring and one nitro group is linked to the other as shown in (c) while in (d) and (e) methoxy is taken place by amino and dimethylamino respectively. In Figure 3 (f), a more complicated derivative is shown where three methoxy groups are linked to one phenyl ring and carboxamidopropane group is connected to the other ring.

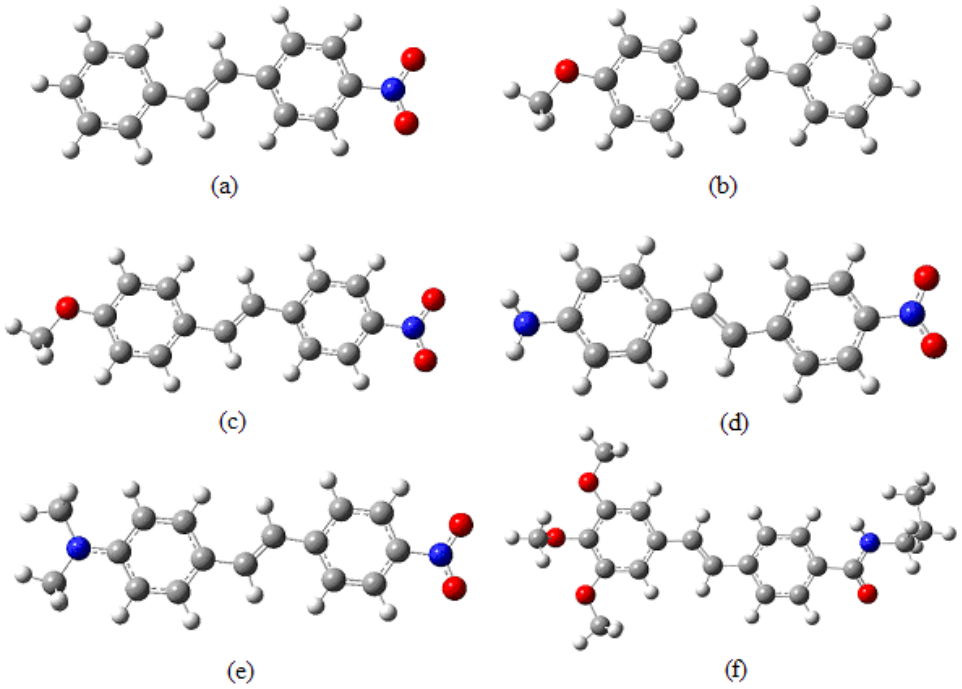



Fig. 3 Geometric structures of stilbene derivatives: (a) trans-4-nitrostilbene; (b) trans-4-methoxystilbene; (c) trans-4-methoxy-4'-nitrostilbene; (d) trans-4-amino-4'-nitrostilbene; (e) trans-4-dimethylamino-4'-nitrostilbene; (f) trans-trimethoxystilbene carboxamidopropane (TMS).

The infrared spectra of the derivatives and their isomers are calculated with B3LYP/6-31G (d) function and the low-frequency part of spectra are shown from Figure 4 (a) to (f). With side groups added to phenyl rings, vibrational modes of stilbene derivatives make appearance in the frequency region of our interest. The strongest vibrational modes of trans- and cis- isomers are quite distinguishable for (a), (b), (d), and (f) which make them promising candidates as functional components in molecular electronic device to process data in long wavelength region. For (a) 4-nitrostilbene, cis- conformation absorbs signal at 25.9 $cm^{-1}$ while trans- conformation absorbs signal at 34.0 $cm^{-1}$. For (b) 4-methoxystilbene, cis- conformation absorbs signal at 26.8 $cm^{-1}$ and trans- conformation absorbs signal at 35.6 $cm^{-1}$. For (d) 4-amino-4'-nitrostilbene, trans-conformation will interact with input wave with frequency at 9.3 $cm^{-1}$ while cis- conformation will interact with input wave with frequency at 24.6 $cm^{-1}$. As for (f) trimethoxystilbene carboxamidopropane (TMS), trans-conformation will reduce the input signal at 18.7 $cm^{-1}$ while cis- conformation will do the same thing to input signal at 33 $cm^{-1}$. Another conclusion we can make from Figure 4 (a) to (f), conformational modification enhanced sensing of stilbene derivatives can be realized because spectral fidelity exists in isomers of various stilbene derivatives.

Strong correlation in vibrational frequencies can be seen between Figure 4 (a) and (b). Three vibrational modes 25.9 $cm^{-1}$ (cis), 29.3 $cm^{-1}$ (cis), and 34.0 $cm^{-1}$ (trans) shown in Figure 4 (a) reappear in (b) and shift simultaneously to higher frequency region at 26.8 $cm^{-1}$ (cis), 31.0 $cm^{-1}$ (cis), and 35.6 $cm^{-1}$ (trans) because the mass of methoxy group in (b) is smaller than that of nitro group in (a). The same correlation can be observed from Figure 8.4 (c) and (d). Four vibrational modes 4.6 $cm^{-1}$ (trans), 22.7 $cm^{-1}$ (cis), and 27.0 $cm^{-1}$ (trans), 28.9 $cm^{-1}$ (cis) in (c) shift to higher frequency region at 9.3 $cm^{-1}$ (trans), 24.6 $cm^{-1}$ (cis), 29.9 $cm^{-1}$ (trans), and 30.8 $cm^{-1}$ (cis) in (d) slightly because the mass of amino group in (d) is smaller than that of methoxy group in (c). If we apply the same correlation to derive spectra of 4-dimethylamino-4'-nitrostilbene from (c) or (d),

vibrational modes in (e) should come from the same modes as shown in (c) or (d) and shift to lower frequency region. However, that is not the case shown in (e) where we have five vibrational modes at 12.0 $cm^{-1}$ (trans), 14.9 $cm^{-1}$ (trans), 21.3 $cm^{-1}$(cis), 28.2 $cm^{-1}$ (cis) and 30 $cm^{-1}$ (trans). Although two vibrational modes of cis- conformation can be predicted from (c) or (d) where 21.3 $cm^{-1}$ (cis) is from 22.7 $cm^{-1}$ (cis) in (c) or 24.6 $cm^{-1}$ (cis) in (d), 28.2 $cm^{-1}$ (cis) is from 28.9 $cm^{-1}$ (cis) in (c) or 30.8 $cm^{-1}$ (cis) in (d), three vibrational modes of trans do not follow the rule. The explanation can be that the effect of structure difference between dimethylamino group and amino group exceeds the effect of mass difference and structures of the side groups will affect the force constant of vibrational modes. Correlation between (f) and others are not easily derived because of its much more complicated structure.

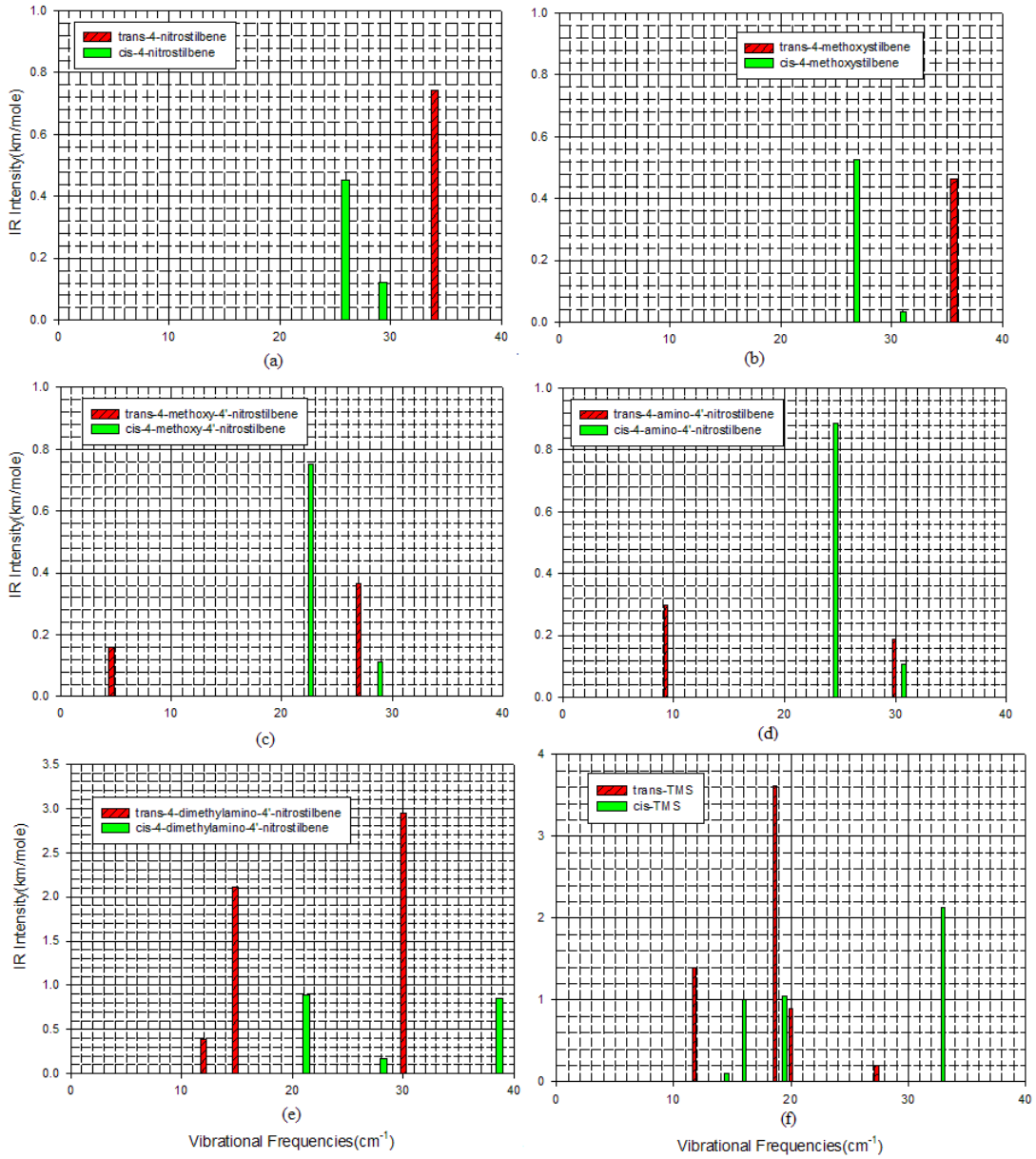


Fig.4 Low-frequency vibrational spectra (< 40 $cm^{-1}$) of trans- and cis- isomers calculated with B3LYP/6-31G (d) function .
Raw frequencies are scaled by 0.96 to eliminate the systematic errors .

Different confirmations of stilbene are studied with the density functional theory (DFT) in gas phase to obtain the potential energies for ground states (S0) and excited states. At first, one-dimensional modeling is executed with torsion angle θ (the rotation around the carbon-carbon double bond C1- C1' ) as the reaction coordinate. These are calculated with B3LYP/6-31G(d) function and the vertical transitions from the ground to state excited state occurs under illumination with a proper frequency. Partial optimization is executed by fixing θ with all the other being modified to lower the energy of a molecule. Optimized trans- and cis-stilbene ground-state structures are the starting points for trans- and cis- sides, respectively. To reveal possible pathways through which isomerization of stilbene occurs, PECs for ground state and first excited state of stilbene are constructed, shown in Fig. 5. There are also two different perpendicular structures from the cis- and trans -side because they evolve from two different starting structures on trans- and cis- side apart which are different in all parameters. After illumination excited cis-stilbene relaxes to a local minimum at θ=40°. On trans- side, the excited trans-stilbene is a minimum in energy.

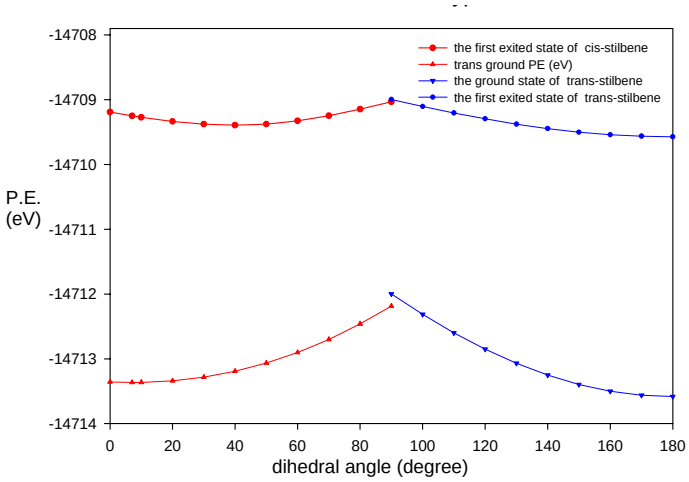



Fig. 5. PEC of the ground and first excited states of trans and cis-stilbene from partial optimization calculations

For two dimensional simulation a torsion angle (θ) and C2-C2' distance is singled out as two reaction coordinates. The reason for using C2-C2' distance as the coordinate is that theoretical and experimental evidences have argued that it plays a major role in tuning the interaction between two phenyl rings. In the equilibrium configurations of trans-, cis- stilbene and DHP, the distances between C2 and C2' are about 5.46 A, 3.25 A and 1.53 A respectively. Fig. 6 is a two dimensional simulation for both C-C distance and torsion angle, showing the potential energy surface of ground and excited state stilbene.

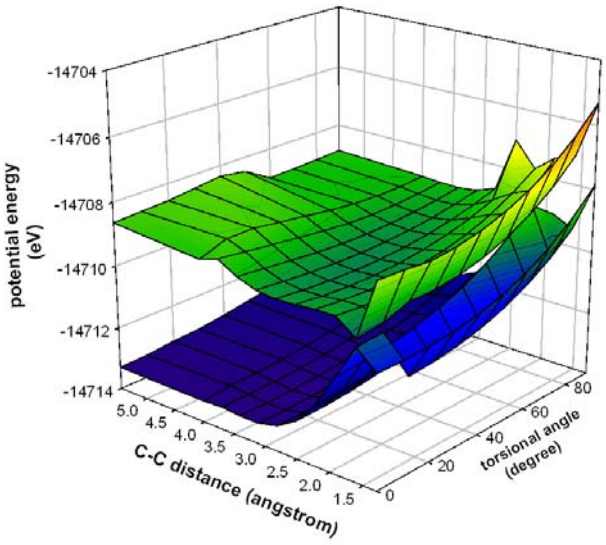



Fig. 6 Potential energy surface of stilbene

During the simulation process, an intermediate structure, dihydrophenanthrene (DHP, showing in Fig. 7), is calculated and optimized, too. The ground state energy simulation result indicates that the potential energy of DHP is only 1.937 eV higher than that of cis-stilbene. Although DHP is a thermally unstable conformation and has not ever been isolated, spectroscopic study in pump-probe experiments has proved its existence via its long wavelength absorption band. DHP reverts to cis-stilbene in the dark and non-oxygen environment in a time ranging from seconds to minutes depending on the ambience. In the presence of oxygen, DHP will get deprived of two hydrogen atoms, turn to phenanthrene (see Figure 8) and can not return to cis-stilbene (see Scheme 9).

The experimental evidence shows that the lifetime of excited cis-stilbene is about 300 fs in gas phase]. It has been observed that excited trans-stilbene has a lifetime of about 80 ps in gas phase, much longer than excited cis-stilbene. These results are natural because the barrier exists in the region of trans configuration.

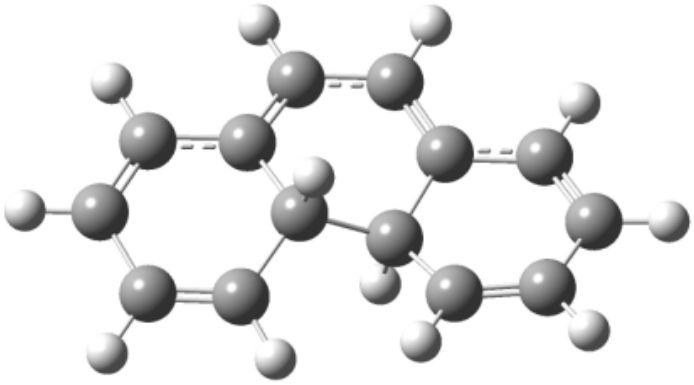
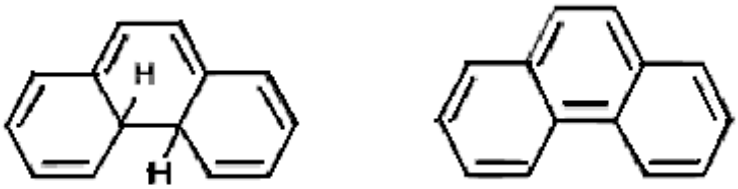


Fig. 7 optimized structure of DHP




**DHP** **phenanthrene**

Figure 8. Schematic structures of (a) DHP and (b) phenanthrene.

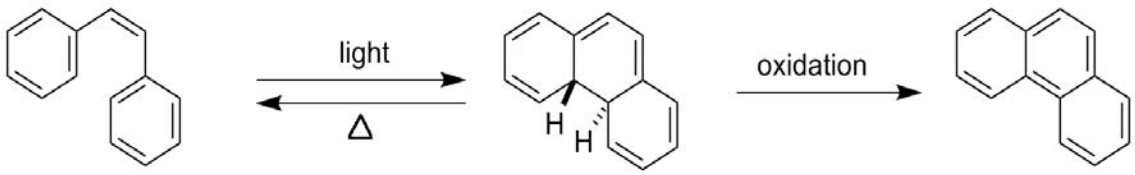
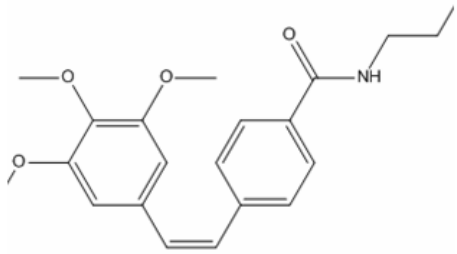


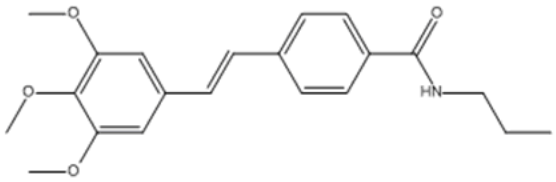

Figure 9. Schematic conversion of cis-stilbene into phenanthrene.

***B. TMS***

Cis- and trans-TMS (Fig 10) are two isomers. They can be converted to each other under light excitation. Simulation on these two isomers was run with B3LYP/6-31G(d) functions using Gaussian 98 package (Fig 11). At the beginning optimization of ground state energy is calculated for cis- and trans-TMS. It proved that the optimized ground state energy for cis-TMS and trans-TMS are -31861.87 eV and -31862.06 eV. Also excited states of optimized cis- and trans- TMS are calculated, for both singlet and triplet, showing in Table I and II. Transition energies along with its corresponding oscillator strengths are displayed.

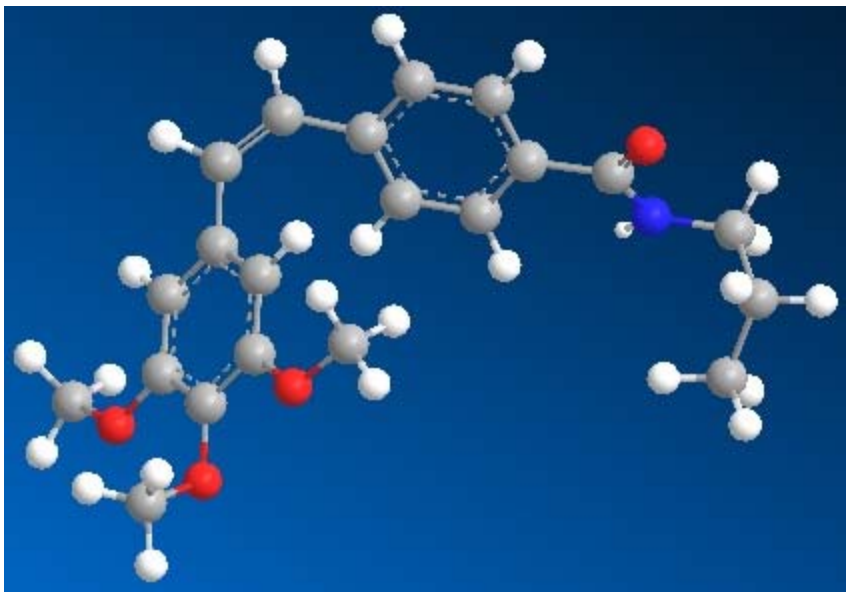



Cis-TMS

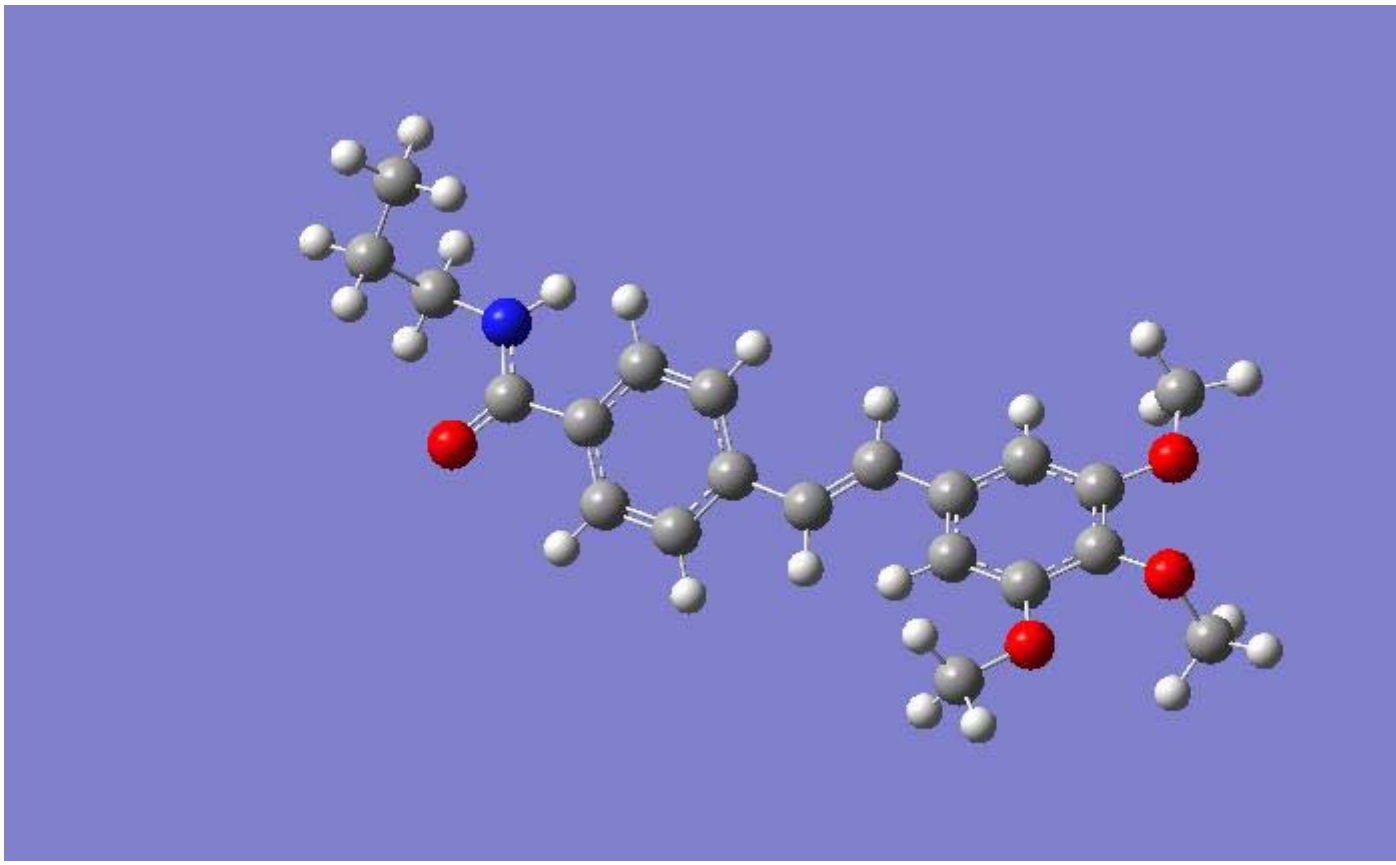



Trans-TMS

Fig. 10 Schematic structure of cis- and trans-TMS



cis-TMS



trans-TMS

Fig. 11 Optimized structure of cis- and trans-TMS

TABLE I: Exciting State Transition Energies (ΔE, eV) and oscillator strengths (f, km/mol) for cis-TMS

| Cis-TMS | Singlet | | Triplet | |
|---|---|---|---|---|
| Exciting State | ΔE | f | ΔE | f |
| 0-1 | 3.8771 | 0.2607 | 2.8820 | 0.0000 |
| 0-2 | 4.0701 | 0.0132 | 3.4992 | 0.0000 |
| 0-3 | 4.5515 | 0.0208 | 3.7279 | 0.0000 |
| 0-4 | 4.7229 | 0.0073 | 4.1205 | 0.0000 |
| 0-5 | 4.8709 | 0.2821 | 4.2221 | 0.0000 |
| 0-6 | 4.9935 | 0.0066 | 4.2838 | 0.0000 |

TABLE II: Exciting State Transition Energies (ΔE, eV) and oscillator strengths (f, km/mol) for trans-TMS

| Trans-TMS | Singlet | | Triplet | |
|---|---|---|---|---|
| Exciting State | ΔE | f | ΔE | f |
| 0-1 | 3.7620 | 0.8652 | 2.5382 | 0.0000 |

| | | | | |
|---|---|---|---|---|
| 0-2 | 3.9931 | 0.0187 | 3.4680 | 0.0000 |
| 0-3 | 4.4240 | 0.0139 | 3.5505 | 0.0000 |
| 0-4 | 4.6274 | 0.0232 | 4.1107 | 0.0000 |
| 0-5 | 4.7441 | 0.3650 | 4.1893 | 0.0000 |
| 0-6 | 4.9369 | 0.0107 | 4.2634 | 0.0000 |

Then these two optimized structures were taken as starting points and all energies as functions of torsion angle were calculated using partial optimization. It proved that ground state energy increases 20eV when the torsion angle increases from 0° to 90° for cis-TMS and this is similar to trans-TMS. Hence this rotation does not provide the optimal path between two isomers. This problem requires additional study.

Similar to stilbene an intermediate structure between cis- and trans-TMS transformations, 2,3,4-trimethoxy-6 -carboxamidopropyl-4a,4b-dihydrophenanthrene (TCD, showing in Fig 12), is captured during the simulation process. The potential energy of TCD is only 1.55 eV higher than that of cis- TMS, showing it is a relatively stable intermediate structure.

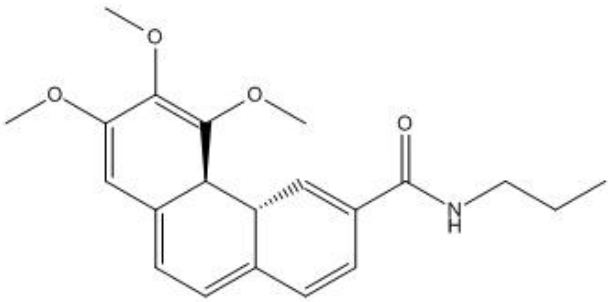



Fig.12. Schematic structure of TCD

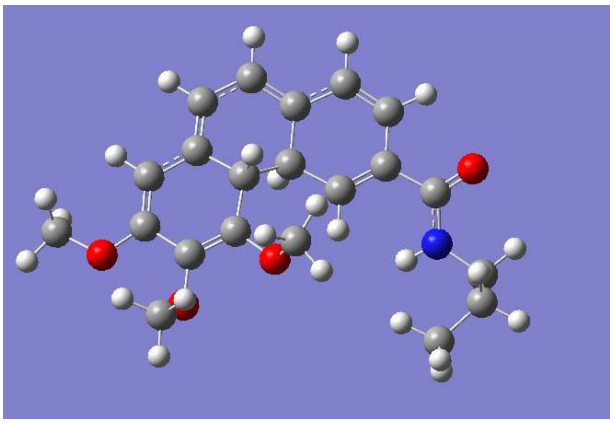


Fig.13. Optimized structure of TCD

One of the most useful characteristics stilbene and its derivatives own is that they are able to form very stable bridged hairpins with DNA. As it is mentioned, TMS-DNA structure is one of the most stable one among various kinds of stilbene-DNA structures. Using Amber 10 package, a TMS-DNA structure, **(TMS-TGCGCA)$_2$**, is optimized to an optimal structure (partial structure shown in Fig 14) .

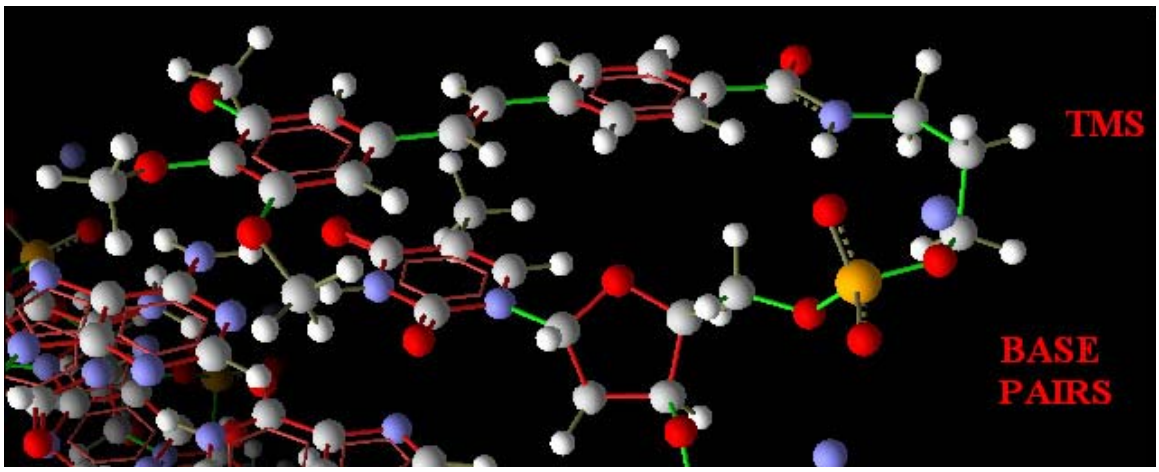



Fig. 14 Partial structure of optimized **(cis-TMS-TGCGCA)$_2$** capping structure

Also by performing normal mode analysis (NMA) over the optimized structure using amber, it is possible to get the oscillator strength against frequency characteristics for both cis-TMS capping with DNA and trans-TMS capping with DNA structures, showing in Fig. 11.

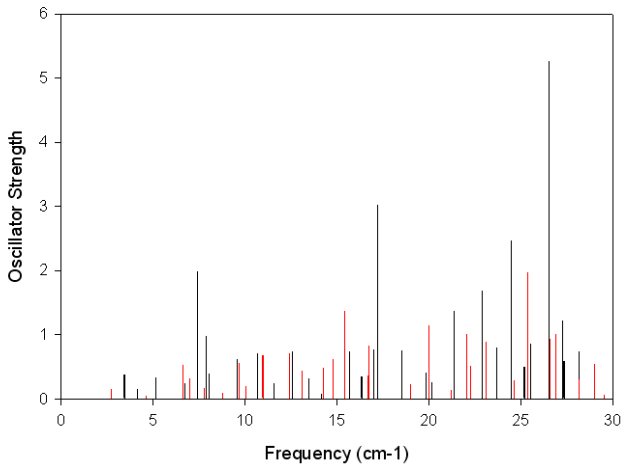



Fig. 15. Oscillator strength vs. frequency for **(cis-TMS-TGCGCA)$_2$** and **(cis-TMS-TGCGCA)$_2$**, shown in black and red bars respectively.

Results of this research have been published in IEEE Transactions on Nanotechnology by Boris Gelmont, Yikan Chen, Zhen Xie, Ying Luo, James Jensen. In the same issue of this journal the paper of Alexei Bykhovski and Dwight Woolard [3] have been published where more detailed analysis of DNA duplex with TMS end capping has been provided.

## 3. Development of a theory for frequency shift: interactions of biological molecules with substrates.

Finding shift of frequencies due to the substrate is one of the challenging problems. In particular molecules can be attracted to the surface without chemical bonding. Such an interaction is responsible for the surface tension. Van der Waals forces are responsible for interaction between molecules and a substrate. The shift in vibrational frefuencies is calculated using MD simulation. Some of the modes are more sensitive to the Van der Waals forces are responsible for interaction between molecules and a substrate than others.

## 4. CONCLUSION

We have performed simulations of potential energy for different isomers of stilbene and its derivatives. In addition to trans and cis- isomers the third isomer has been found and optimized. These results suggest that stilbene and TMS, as effective covalent linkers to DNA, are strong candidates for multi-state spectral sensing technology due to their distinct differences of vibrational frequencies of different isomers.

REFERENCES

1. Robert L. Letsinger and Taifeng Wu, Use of a Stilbenedicarboxamide Bridge in Stabilizing,Monitoring, and Photochemically Altering Folded Conformations of Oligonucleotides, J. Am. Chem. Soc. 1995,117, 7323-7328

2.Zeynep Dogan, Ralph Paulini, Jan A. Rojas Stutz, Sukunath Narayanan, and Clemens Richert, 5'-Tethered Stilbene Derivatives as Fidelity- and Affinity-Enhancing Modulators of DNA Duplex Stability, J. Am. Chem. Soc. 9, 126, NO. 15, 2004 4763

3.J. Tuma, R. Paulini, J. A. R. Stutz and C. Richert, How Much π-Stacking Do DNA Termini Seek? Solution Structure of a Self-Complementary DNA Hexamer with Trimethoxystilbenes Capping the Terminal Base Pairs, Biochemistry, 2004, 43, 15680–15687

4. Alexei Bykhovski and Dwight Woolard "Hybrid Ab-Initio/Empirical Approach To Study Conformations and Light-Induced Transitions In Stilbene-DNA Structures", IEEE Transactions on Nanotechnology, Volume: 9. Issue: 5, page(s): 565 – 574, 2010

## Publications.

1.X. Li, T. Globus, B. Gelmont, L. C. Salay, and A. Bykhovski, "Terahertz Absorption of DNA Decamer Duplex", Journal of Physical Chemistry A, v.112, #47, , pp.12090-12096 , 2008
DOI: 10.1021/jp806630w

2. Boris Gelmont, Ramakrishnan Parthasarathy, Tatiana Globus, Alexei Bykhovski, and Nathan Swami, "Terahertz (THz) Electromagnetic Field Enhancement in Periodic Subwavelength Structures" , IEEE Sensors Journal, 8,6,791-6 (2008).
DOI: 10.1109/JSEN.2008.923222

3. B. Gelmont, R. Parthasarathy, T. Globus," Edge effects in propagation of terahertz radiation in subwavelength periodic structures", Semiconductors , 42,8,924-30,(2008).
PACS: 41.20.Jb, 78.68.+m, 78.70.Gq,

4. Boris Gelmont, Yikan Chen, Zhen Xie, Ying Luo, James Jensen, "Stilbene and Its Derivatives for Multi-State Spectral Sensing", IEEE Transactions on Nanotechnology, Volume: 9. Issue: 5, page(s): 558 – 564, 2010
DOI: 10.1109/TNANO.2010.2050210

5. Alexei Bykhovski, Boris Gelmont, "Modeling of Variability of Terahertz Spectra of Biological Molecules Caused by Chemical Interactions, Concentration Effects and Temperature", The Journal of Physical Chemistry **B** 114 (38), 12349-12357,2010
DOI: 10.1021/jp101510k

6.Tatiana R. Globus, Michael L. Norton, Maryna I. Lvovska, Derek A. Gregg, Tatyana B. Khromova, Boris L. Gelmont, **"**Reliability Analysis of THz Characterization of Modified and Unmodified Vector Sequences", IEEE Sensors Journal, VOL. 10, NO. 3, 410-8, 2010.
DOI: 10.1109/JSEN.2009.2038122

7.Boris Gelmont, Tatiana R. Globus, **"**Edge effects in perfectly conducting periodic subwavelength structures", IEEE Transactions on Nanotechnology, v.10, NO. 1, 83-87,January 2011
DOI: 10.1109/TNANO.2010.2064785

8. Boris Gelmont, Yikan Chen, Zhen Xie, Ying Luo, James Jensen, **"**Stilbene and Its Derivatives for Multi-State Spectral Sensing", 2009 Nanoelectronic Devices for Defense & Security (NANO-DDS) , Fort Lauderdale ,FL, September 2009.

9.Boris Gelmont, Tatiana R. Globus, **"**Edge effects in perfectly conducting periodic subwavelength structures", 2009 Nanoelectronic Devices for Defense & Security (NANO-DDS), Fort Lauderdale ,FL, September 2009.

10. Alexei Bykhovski, Boris Gelmont, "The Influence of Environment on THz Absorption of Biological Threat Agents" , ISSSR 2010 Springfield, Missouri ,June 21 - 24, 2010.

11. Tatiana Globus, Boris Gelmont, C. Neal Stewart, Reginal J. Millwood, Michael L. Norton , "Terahertz Spectroscopic Signature From Short Artificial DNA Molecules with Well Controlled Structure", ISSSR 2010, Springfield, Missouri ,June 21 - 24, 2010.

12.B. Gelmont THz Science & Tehcnology: Stilbene and Its Derivatives for Multi-State Spectral Sensing, EDSDS Workshop, Raleigh, NC, 3/18-20/2009

13. Boris Gelmont,"THz Science & Tehcnology: Stilbene and Its Derivatives for Multi-State Spectral Sensing",MURI Meeting,Washington,DC, July 13-14,2011