# REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggesstions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA, 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any oenalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.
PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

| 1. REPORT DATE (DD-MM-YYYY) | 2. REPORT TYPE | 3. DATES COVERED (From - To) |
|---|---|---|
| 31-08-2008 | Final Report | 1-Oct-2002 - 31-May-2008 |

| 4. TITLE AND SUBTITLE | 5a. CONTRACT NUMBER |
|---|---|
| Computational Modeling of Light Induced Transformations in Organic Molecule | DAAD19-02-1-0439 |
| | 5b. GRANT NUMBER |
| | 5c. PROGRAM ELEMENT NUMBER 4Y1012 |

| 6. AUTHORS | 5d. PROJECT NUMBER |
|---|---|
| B.Gelmont | 611102 |
| | 5e. TASK NUMBER 622622 |
| | 5f. WORK UNIT NUMBER 622622 |

| 7. PERFORMING ORGANIZATION NAMES AND ADDRESSES | 8. PERFORMING ORGANIZATION REPORT NUMBER |
|---|---|
| University of Virginia Office of Sponsored Programs 1001 N. Emmett St.  P.O. Box 400195 Charlottesville, VA      22904  -4195 | 662262 |

| 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) | 10. SPONSOR/MONITOR'S ACRONYM(S) ARO |
|---|---|
| U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211 | 11. SPONSOR/MONITOR'S REPORT NUMBER(S) 44520-EL.1 |

## 12. DISTRIBUTION AVAILIBILITY STATEMENT

Approved for Public Release; Distribution Unlimited

## 13. SUPPLEMENTARY NOTES

The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

## 14. ABSTRACT

The goal of this research is to investigate theoretically and experimentally the feasibility of a new Multi-State Spectral Sensing (MS3) concept where bio-signature information can be collected from multiple metastable conformations for enhanced sensing in the THz region. Several geometric isomeric molecular systems have been investigated including 2-butenes, retinals, and stilbenes, in order to 1) study THz spectra of different molecular conformations ; 2) illustrate a basic procedure through which optical excitation can be used to modify molecular conformations; 3) study possible binding of stilbene or its derivatives to DNA terminal. We have conducted the initial theoretical investigation of emission of radiation by DNA

## 15. SUBJECT TERMS

photoisomerization, trans- and cis-isomers,retinal, stilbene, THz spectra, DNA , $CO_2$ lasers

| 16. SECURITY CLASSIFICATION OF: | | | 17. LIMITATION OF ABSTRACT | 15. NUMBER OF PAGES | 19a. NAME OF RESPONSIBLE PERSON Boris Gelmont |
|---|---|---|---|---|---|
| a. REPORT U | b. ABSTRACT U | c. THIS PAGE U | SAR | | 19b. TELEPHONE NUMBER 434-924-6090 |

Standard Form 298 (Rev 8/98)
Prescribed by ANSI  Std. Z39.18

## Report Title

Computational Modeling of Light Induced Transformations in Organic Molecule

## ABSTRACT

The goal of this research is to investigate theoretically and experimentally the feasibility of a new Multi-State Spectral Sensing (MS3) concept where bio-signature information can be collected from multiple metastable conformations for enhanced sensing in the THz region. Several geometric isomeric molecular systems have been investigated including 2-butenes, retinals, and stilbenes, in order to 1) study THz spectra of different molecular conformations ; 2) illustrate a basic procedure through which optical excitation can be used to modify molecular conformations; 3) study possible binding of stilbene or its derivatives to DNA terminal. We have conducted the initial theoretical investigation of emission of radiation by DNA components upon the absorption of infrared (IR) radiation. The anharmonicity is responsible for coupling of the oscillators and the energy transfer. The Fermi resonances provide the most effective channels of the energy transfer. For the absorption bands evaluated with the HF model the probabilities of Fermi resonance induced transitions are calculated.

## List of papers submitted or published that acknowledge ARO support during this reporting period.  List the papers, including journal references, in the following categories:

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

1.Dwight L. Woolard , Ying Luo, Boris L. Gelmont,  Tatiana Globus, and  James O. Jensen, ” Bio-Molecular Inspired Electronic Architectures for Enhanced Sensing of THz- Frequency Bio-Signatures”, International Journal of High Speed Electronics and Systems(IJHSES), Vol. 16,No. 2, pp. 609-637 (2006).
2. T.J. Wright, Ying Luo, Tatiana Globus, Boris Gelmont, Tatyana Khromova, and Acar Isin, “ THz Characterization of All-Trans and 9 Cis Retinal: Experiment and Modeling”, IEEE Sensors Journal, 8,6,781-6 (2008).
3. T. Globus, T. Khromova, A. Bykhovski, B. Gelmont, and D. Woolard, Terahertz Sensing of Bio-Water Contaminants Using Vibrational Spectroscopy, Int. J. High Speed Electr. Systems, Water & Frontier issue, accepted for publication (2007).

**Number of Papers published in peer-reviewed journals:**          3.00

### (b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Raphael P. Moon,Boris Gelmont,"Laser Induced Millimeter Wave Fluorescence From Bio-Materials",CB Defense Technology Watch Newsletter.

**Number of Papers published in non peer-reviewed journals:**          1.00

### (c) Presentations

1. “A Bio-Molecular Architectural Concept for Enhanced Sensing of Bio-Signatures”, ARO workshop on Terahertz Sensing Science and Technology, April 27, 2004
2."THz & Switching Characteristics of Organic Molecules & Nanostructures",DTRA Program on “Advanced Architectures for Biological Agent Detection & Discrimination”, Hoboken, NJ ,January 8-10, 2007
3. "THz & Switching Characteristics of Organic Molecules & Nanostructures", ARO Mid-year Review, Duck Key, FL, December,3-5,2008

**Number of Presentations:**     3.00

### Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

**Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):**          0

### Peer-Reviewed Conference Proceeding publications (other than abstracts):

1. Y.Luo, B. Gelmont, and D. Woolard, "A Bio-Molecular Architectural Concept for Enhanced Sensing of Bio-Signatures", 58th OSU International Symposium on Molecular Spectroscopy, June 16-20,2003 .

2. D. Woolard , Y.Luo, and B. Gelmont, "A Bio-Molecular Electronic Architecture Based Upon Electro-TH-Optical Characteristics", 3rd International Conference on Computational Modeling and Simulation of Materials. Acireale, Sicily, Italy, May 29 to June 4, 2004, invited.

3. D. Woolard, Y.Luo, B.Gelmont , and T.Globus, "A Bio-Molecular Architecture in THz Region Based Upon Photo-Optical Transition", Terahertz Sensing & Electronic Technology Meeting SPIE Conference on Chemical and Biological Standoff Detection II (OE120), 25-28th of October, 2004 , Philadelphia.

4.Dwight L. Woolard , Ying Luo, Boris L. Gelmont,  Tatiana Globus, and  James O. Jensen, " Bio-Molecular Electronic Architectures for Enhanced Sensing of THz-Frequency Bio-Signatures", invited ,Advanced Workshop on Frontiers in Electronics (WOFE), Aruba, December 19-23, 2004.

5. D. Woolard, Y.Luo, B.Gelmont and T. Globus "A Bio-Molecular Inspired Electronic Architecture ", SPIE Defense and Security Symposium , Proceedings of  SPIE, v.5790-23, Terahertz for Military and Security Applications III, Orlando, Florida, March 28- April 1, 2005, invited.

6. Y.Luo, D. Woolard, and B. Gelmont, "Simulations of retinal-based electronic components for application to THz frequency sensing platforms", SPIE Defence & Security Symposium, Terahertz for military and security applications IV, Orlando, April 17-21, 2006, SPIE Paper Number: 6212-12.

7. B. Gelmont, Y. Luo, A. Bykhovski, T. Globus, D. Woolard, R. Moon, N. Green, I. Alexeev, LASER Induced Millimeter/Sub-Millimeter Wave Radiation From Bio-Materials, Proceedings of 7th Joint Conference on Standoff Detection for CB Defense (2006).

8. T.J. Wright, Ying Luo, Tatiana Globus, Boris Gelmont, Tatyana Khromova, and Acar Isin, " THz Characterization of All-Trans and 9- Cis Retinal: Experiment and Modeling", 2007 Nanoelectronic Devices for Defense & Security Conference.

9. Ying Luo, Dwight L. Woolard ,"THz Spectra Studies of the Isomers of Stilbene Derivatives and  Their Application for Enhanced Sensing at the Nanoscale ",
2007 Nanoelectronic Devices for Defense & Security Conference.

10. Zhen Xie, Alexei Bykhovski, Boris Gelmont, Tatiana Globus, James Jensen"Computational Modeling of the Molecular Complex Formed by DIPAIN II And T-2 Toxin", 2008 International Symposium for Spectral Sensing Research

**Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):**        10

---

# (d) Manuscripts

**Number of Manuscripts:**        0.00

---

**Number of Inventions:**

---

## Graduate Students

| NAME | PERCENT_SUPPORTED |
|------|------|
| Ying Luo | 0.20 |
| **FTE Equivalent:** | **0.20** |
| **Total Number:** | **1** |

## Names of Post Doctorates

| NAME | PERCENT_SUPPORTED |
|------|------|
| Gregory Recine | 0.10 |
| **FTE Equivalent:** | **0.10** |
| **Total Number:** | **1** |

## Names of Faculty Supported

| NAME | PERCENT_SUPPORTED | National Academy Member |
|------|------|------|
| Alexei  Bykhovski | 0.30 | No |
| Boris Gelmont | 0.40 | No |
| **FTE Equivalent:** | **0.70** | |
| **Total Number:** | **2** | |

## Names of Under Graduate students supported

| NAME | PERCENT SUPPORTED |
|---|---|
| **FTE Equivalent:** | |
| **Total Number:** | |

## Student Metrics
This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: ...... 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

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

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense ...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:...... 0.00

## Names of Personnel receiving masters degrees

| NAME |
|---|
| Ying Luo |
| **Total Number:**          **1** |

## Names of personnel receiving PHDs

| NAME |
|---|
| Ying Luo |
| **Total Number:**          **1** |

## Names of other research staff

| NAME | PERCENT SUPPORTED |
|---|---|
| **FTE Equivalent:** | |
| **Total Number:** | |

## Sub Contractors (DD882)

# Inventions (DD882)

# Computational Modeling of Light Induced Transformations in Organic Molecule

Principal Investigator/Project Manager:        Boris Gelmont

PI/PM Contact Info:        University of Virginia
Department of ECE
( 434)-924-6090
 e-mail: gb7k@Virginia.edu

Project Period:        01 October 2002 to May 31 2008

Prepared by:

Boris Gelmont[1]
Raphael Moon[2]

[1]University of Virginia, ECE Department, [2]US Army, ECBC,

FINAL REPORT
August 2008

**ABSTRACT**

The goal of this research is to investigate theoretically and experimentally the feasibility of a new Multi-State Spectral Sensing (MS3) concept where bio-signature information can be collected from multiple metastable conformations for enhanced sensing in the THz region. Several geometric isomeric molecular systems have been investigated including 2-butenes, retinals, and stilbenes, in order to 1) study THz spectra of different molecular conformations ; 2) illustrate a basic procedure through which optical excitation can be used to modify molecular conformations; 3) study possible binding of stilbene or its derivatives to DNA terminal. We have conducted the initial theoretical investigation of emission of radiation by DNA components upon the absorption of infrared (IR) radiation. The anharmonicity is responsible for coupling of the oscillators and the energy transfer. The Fermi resonances provide the most effective channels of the energy transfer. For the absorption bands evaluated with the HF model the probabilities of Fermi resonance induced transitions are calculated.

# Switching Characteristics of Organic Molecules Nanostructures in THz Region

This work is the part of a broad research on bio-molecular-based device concepts for enhanced sensing Terahertz (THz) frequency bio-signatures. The overall Project Goal is to study Electro-THz-optical processes within bioelectronic devices and systems.

This research seeks to define a new architectural paradigm whereby enhanced sensing of terahertz(THz)-frequency biological(bio)-signatures may be achieved. Here, the basic methodology is to incorporate the target bio-molecular agents directly into the electronic architecture and to utilize their THz-frequency characteristics directly into the function of the sensor platform. This report will illustrate how new sensor platforms can utilize combinations of THz, and optical, or Electro-THz-Optical (ETO), based communication and control to refine the process of collecting THz bio-signatures and to define approaches for increasing the available number of THz spectral features through a procedure that will be referred to as Multi-State Spectral Sensing ($MS^3$). The introduction of $MS^3$ is of significant importance because the number of spectral signature features associated with any individual bio-agent in its natural state (i.e., ground state) is somewhat limited and new methods are needed to provide for adequate levels of agent discrimination.

The new concepts for a bio-molecular based sensing architecture presented in this research were motivated almost exclusively by prior research into the utilization of terahertz (THz) frequency spectroscopy as a potential tool for the detection of biological materials and agents [1]. Indeed, nearly ten years ago, our group initiated new scientific studies into the fundamental interactions of THz radiation with biological materials at the molecular level. This has been followed by a continuous and focused effort to establish a new THz sensing science and technology base that can be used to assess the detection, identification and characterization capability of THz spectroscopic analysis. Obviously, these activities were made a high priority because THz sensing has important potential relevance to both military and homeland defense against bio-based threats. However, the spectral probing of the fine structural and electronic characteristics of organic molecules also has the potential to provide new insights into microscopic biological systems and therefore may also have broad ramifications to biological and medical science in the future.

The first step in the realization of the proposed integrated sensor architecture is a detailed theoretical description of the target bio-molecules, and the associated ETO-based processes, that are required for defining communication and control at the nanoscale. Hence, this report presents modeling and simulation results for an initial set of bio-molecules (e.g., butane, retinal, stilbene) that: (a) illustrates a procedure through which optical excitation can be used control the molecular conformational state, and (b) accurately predicts the THz spectral characteristics in both the natural (i.e., ground) state and the final metastable state. Therefore, this research is establishing a new scientific foundation of knowledge which can serve as a blueprint for enabling integrated bio-molecular sensing platforms of the future with enhanced capabilities for sensing and processing THz bio-signatures. Finally we study possible binding of stilbene or its derivatives to DNA terminal.

Many organic and bio- molecules have one or more metastable conformational states besides the stable state. Different states have different structural conformations with distinct vibrational spectra. The photo-induced transitions stimulate the switch between these states that will yield remarkable differences to the phonon-induced absorption characteristics at THz region. These

unique spectral characteristics of molecules can be used to design molecule-based electronic devices. The most well known opportunity is to study molecules with two conformational states: cis- and trans- with different transmission spectral characteristics in THz region. Our goal is to study the photo-induced transitions from trans- to cis-geometry . This photo-induced transition occur with a great change of molecule geometry that should yield remarkable differences to the phonon-induced absorption characteristics at terahertz frequencies.

## 1.1. Trans/Cis 2-butene

To understand the basic transformation processes and the viable options for theoretical analysis it is instructive to first consider simple molecules. For our first  simulation, butene has been chosen as a very simple molecule with typical trans to cis isomerization around a double carbon bond. Trans-2-butene and cis-2-butene are geometric isomers, a type of stereoisomerism in which atoms or groups display orientation differences around a double bound or ring  (Fig.1).



Figure 1. Geometric structures of trans- and cis- 2-butene.

Molecular geometries of cis-2-butene and trans-2-butene are both taken from organic molecule database of Matt Repasky (http://zarbi.chem.yale.edu/~matt/) and all calculation are done in Gaussian98 package [2]. We calculated the energies of the ground states with restricted Hartree-Fock method (RHF). The energies of the excited states are found within the configuration interaction approach, modeling excited states as combinations of single substitutions out of the Hartree-Fock ground states.
To monitor the process of isomerization from cis-2-butene to trans-2-butene, we took the C1-C2-C3-C4 torsional angle $\theta$ to be the reaction coordinate. This angle was constrained at a fixed value between $0^o$ and $180^o$ but other coordinates are free during the optimization of the corresponding molecular structure.  As a result  of the isomerization process the dihedral angle changes from $\theta=0$ which corresponds to cis-2-butene to $\theta=180$ related to trans -2-butene for the ground ($S_0$) and first excited singlet state ($S_1$).  The isomerization process shows a large energy barrier in the ground state (1.91 eV between $\theta=0^o$ and $\theta=90^o$, 1.9804 eV between $\theta=90^o$ and $\theta=180^o$). There is no barrier in the first excited singlet state, which is ideal for an ultrafast switch between the two stable states, cis and trans isomer. But the excitation energy from $S_0$ to $S_1$ (8.487 eV for cis-2-butene and 8.465 eV for trans-2-butene) is big compared with the energy of visual photons (Fig.2).

We also calculated the vibrational frequencies of both cis-2-butene and trans-2-butene. Vibrational frequencies are computed by determining the second derivatives of the energy with respect to the Cartesian nuclear coordinates and then transforming to mass-weighted coordinates. We obtained the big difference in the vibrational spectra of cis- and trans-2-butene.
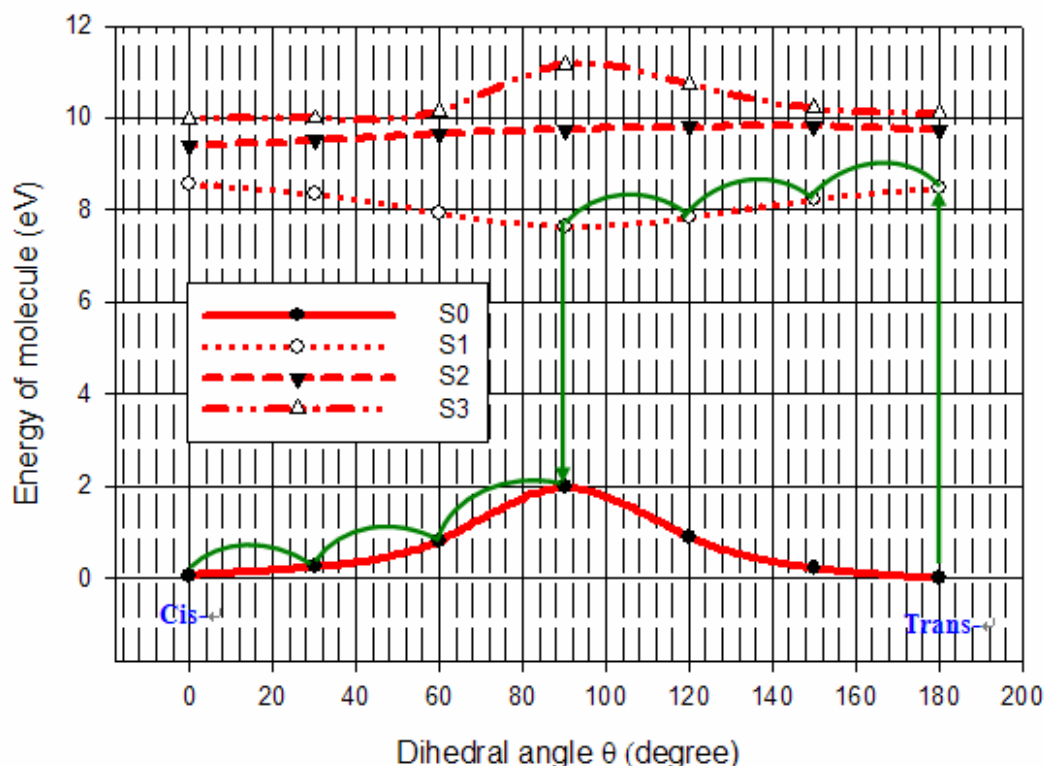


Figure 2. Photo-induced isomerization process of butene isomers

## 1.2. Retinal Isomers

The primary event in vision process is the photoisomerization of 11-cis-retinal, the chromophore of rhodospin, to all-trans-retinal. The process is completed in only 200 fs and has a quantum yield 0.67. The retinal has two properties which make it very interesting to us. First, it is an aromatic system, which means the double bonds form large orbitals that extend over the whole molecule and the electrons in these orbitals can be excited by light easily. The electrons in retinal can absorb photons in the visible range of wavelengths (400-800 nm). Secondly, the double bonds of retinal can isomerize upon absorption of photons from 11-cis-retinal to all-trans-retinal, which makes it possible to detect the process by measuring characteristics of these two isomers. We modeled the photoisomerization process of the isolated retinal. We calculated the potential energy vs torsion angle for the ground state $S_0$ with Restricted Hartree-Fock (RHF) method and

6

density functional theory (DFT) . By including some of the effects of electron correlation, DFT method achieves greater accuracy than Hartree-Fock method at an increase in cost of time . Calculations of the potential energy in the ground state $S_0$ for all three isomerizations, 9-cis/all-trans, 11-cis/all-trans and 13-cis/all-trans, were carried out with ab initio molecular orbital methods within both Hartree-Fock (HF) and density functional theory (DFT) methods with the split valence polarized 6-31G* basis set using the GAUSSIAN 98 package. The B3LYP density functional was used, which is Becke's three parameter hybrid functional using the Lee, Yang, and Parr (LYP) correlation functional. The electronic excited-state energies were calculated with TDDFT method to estimate the necessary optical excitation.

The rotation is possible about three different carbon double bond. The double bonds of retinal can isomerize upon absorption of photons from all-trans-retinal to 9-cis-retinal , 11-cis-retinal , or 13-cis-retinal (Fig.3).

We have taken the torsional angles $\theta$ of C8-C9-C10-C11, C10-C11-C12-C13, and C12-C13-C14-C15 as the reaction coordinates respectively. These angles were constrained at a fixed value from $0^o$ to $180^o$ but other coordinates are free during the optimization of the corresponding molecular structure. $\theta = 0^o$ represents the corresponding cis isomer, i.e. 9-cis, 11-cis or 13-cis retinal in three isomerizations and $\theta = 180^o$ corresponds to all-trans-retinal in all three isomerizations. The potential energy vs torsion angle of isomerizations around C9=C10, C11=C12, and C13=C14 have been calculated with HF and DFT methods. The results calculated with HF method agree with the results calculated with DFT method qualitatively. For both HF method and DFT method, all-trans-retinal has the smallest energy among all these four isomers. We have also found that 9-cis and 13-cis isomers happen to have the same energy with both HF and DFT methods. According to our calculations, if we go from cis to trans isomers, the isomerization from 11-cis to all-trans retinal has the smallest barrier among these three processes. And contrarily if we go from trans to cis isomers, the isomerization from all-trans to 13-cis retinal has the smallest barrier compared with the other two processes (Fig.4).

We have calculated the excitation energies of these four isomers. The energies of the excited states are found within both the configuration interaction approach (CIS) and time-dependent DFT method (TDDFT).

Actually, singlet excited states are not the lowest excited states we could obtain from calculation. We got several triplet excited states between the ground state and the first singlet excited states but the dipole moments and oscillator strengths for these transitions are 0, which means the transitions to these triplet excited states are forbidden. For molecules with low lying excited states, TDDFT makes a considerable improvement over Hartree-Fock based methods (like CIS). The smaller excitation energies in the excited states (ca. 3~4eV) in comparison with butene make excitations of retinal isomers in the ground state $S_0$ much easily realized by absorption of a proper photon than cis/trans 2-butene. According to our calculations, the lowest excitation energies of the four isomers are relatively close to one another so it is a big challenge how to excite only one isomer. The possible answer is to choose a proper environment where isomers will be but further investigation has not been done yet.
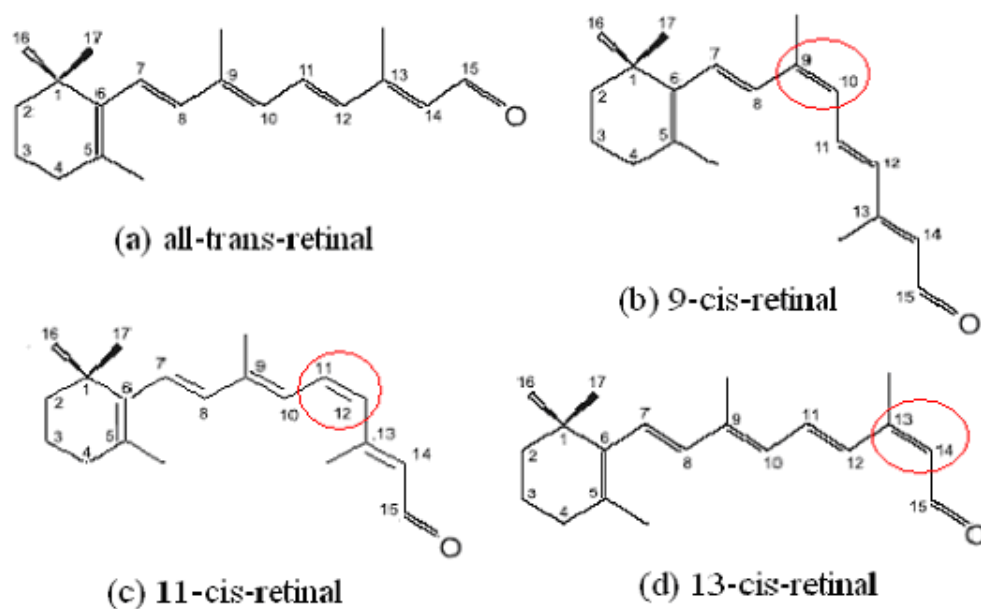
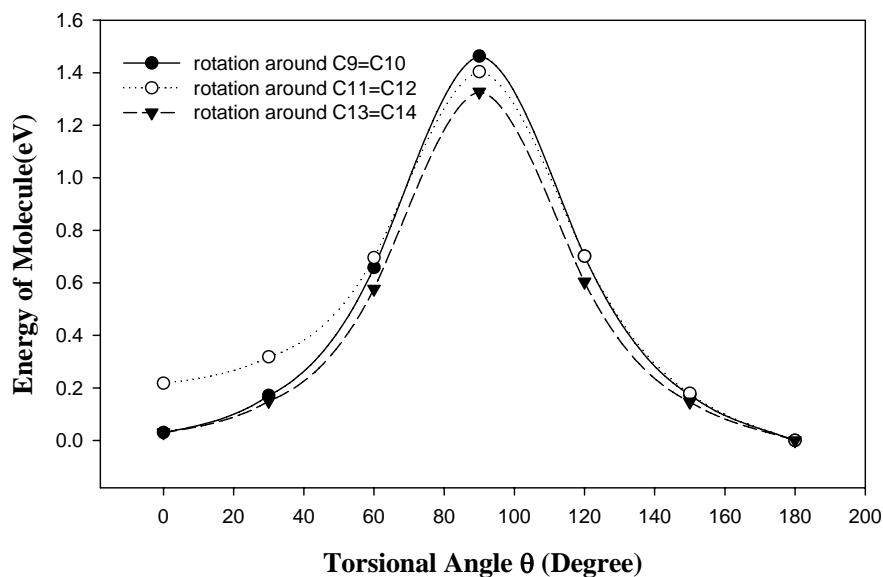Figure 3. Geometric structures of retinal isomers



Figure 4. PECs of the ground state of all-trans-retinal rotated around C9=C10, C11=C12, and C13=C14 double bonds at DFT level.

The calculations of the vibrational frequencies and infrared intensities (Fig.5-7) were carried out with HF/6-31G* method . Due to the neglect of electron correlation, frequency values computed at the Hartree-Fock level are overestimated about 10%-12%. In addition because of the choice of a medium-sized basis set, our values must be expected to deviate even a bit more from

experiment (by around 15% in all). Therefore, we scaled our calculation of frequencies by an empirical factor of 0.893 to eliminate known systematic errors.

Both all-trans-retinal and 9-cis-retinal have been studied experimentally in order to characterize THz spectra in both the ground state and the metastable state and to derive the correlation between the experimental measurements and simulation results. To investigate the impact of external optical excitation on the THz spectra, the original FTIR system was modified to include an off axis excitation source inside the sample chamber and excitation sources was selected according to the simulation results. The observed variations in transmission spectra are rather small. However the experimental results demonstrate that it is possible to detect conformation change in retinal molecules using THz spectroscopy.



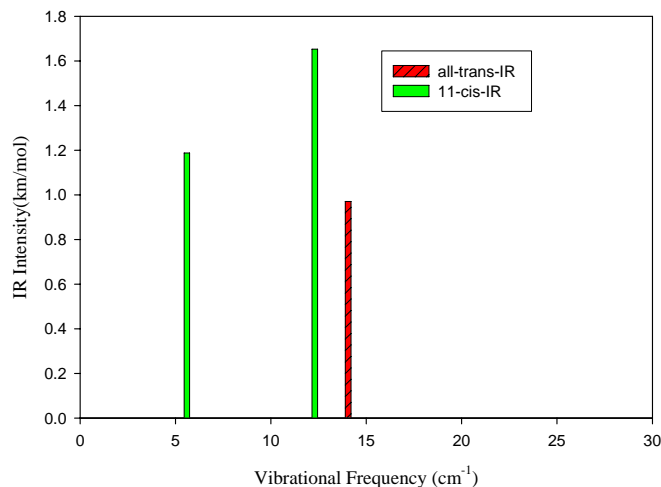Figure 5. FIR spectra of 9-cis-retinal and all-trans-retinal ($<30$ cm$^{-1}$)



Figure 6. FIR spectra of 11-cis-retinal and all-trans-retinal ($<30$ cm$^{-1}$)
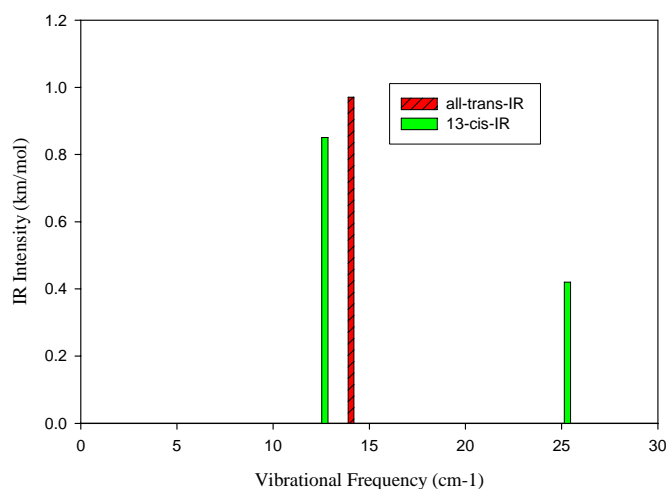
Figure 7 . FIR spectra of 13-cis-retinal and all-trans-retinal ($<30$ cm$^{-1}$)

For the fabrication of retinal-based sensors the retinal has to be attached to solid substrate. The next problem has to be solved is a choice of the proper substrate and possible techniques for the retinal attachment. Monolayers of retinal immobilized on solid substrates are of considerable importance not only for applications as retinal-based sensors but also for investigations of the complex behavior of retinal molecules at interfaces. By modifying one end of retinal with a thiol linker, we could chemically graft the retinal to gold surfaces. Two-dimensional gold nanostructure arrays can be produced by depositing gold onto pit-patterned highly oriented pyrolytic graphite (HOPG) surface. It is also shown that the two-dimensional spatial distribution of gold nanostructures can be controlled and that various shapes and sizes of gold nanostructures can be produced.  It is also possible to produce gold nanostructures on other substrates such as Si.

   Cysteine is an amino acid with an amino group ($-NH_2$) at one end and a thiol group (-SH) at the other end. Retinal can be connected to cysteine by reaction between the acyl (Carbonyl) group (-HC=O) and the amino group. The thiol group (-SH) in the resultant retinal derivative will chemically graft retinal to gold surfaces.  To understand the complex behavior of retinal monolayers at interfaces, we have begun our investigation of the molecular system where one retinal isomeric molecule is connected to a gold atom via the link of a cysteine molecule (retinal- amino -Au).

We have made  simulation of ground state energies and very far infrared spectra of the retinal isomeric molecule connected to a gold atom via the link of a cysteine molecule  (retinal- amino - Au). All calculations were carried out in Gaussian 98 package. Energies and vibrational frequencies were calculated with density functional theory (DFT) utilizing LANL2DZ basis set. B3PW91 is used at the DFT level, which is based on Becke-3 hybrid exchange functional and the Perdew-Wang 91 correlation functional. Excited states were calculated with time-dependent DFT (TDDFT) method.

   The very far infrared spectra ($<30$cm$^{-1}$) of all-trans-retinal- amino -Au, 9-cis-retinal- amino -Au, 11-cis-retinal- amino -Au, 13-cis-retinal- amino -Au have been calculated. The strongest peaks of 9-cis (17 cm$^{-1}$) and 11-cis (24 cm$^{-1}$) retinal derivatives are distinguishable from that of all-trans (21 cm$^{-1}$); however, the strongest peak of 13-cis retinal derivative is close to that of all-trans. It

10

follows from our calculation that there are more vibrational modes in FIR spectra of retinal derivatives than those of isolated retinal isomers. The spectra fidelity of retinal isomers exists in retinal derivatives, which can be used in defining multiple communication channels and for realizing the MS³ (Multi-State Spectral Sensing ) approach to expand the amount of bio-signature information.

Nevertheless there are two reasons that drive us to investigate other candidates besides retinal. First, there are so many double bonds in the chain of retinal molecules that it is difficult to control switching. Second, the lowest excitation energies of allowable states of different retinal isomers are very close which means the specific isomerization can not be controlled only by light sources and other conditions have to be explored to control the isomerization around the specific double bond.

## 1.3. Stilbene and its Derivatives

In addition to retinal isomers, stilbene isomers have also been considered as an alternative approach to bio-devices. Stilbenes are another extensively studied geometric isomers. As representative examples of such compounds, stilbenes are mostly studied for understanding photoisomerizations across double bonds. Photoisomerization of stilbenes involves (pi, pi*) excited states. Most of stilbenes absorb in theUV region and will absorb in the visible region by introducing polar substituents as electron delocalizing groups into the stilbene structures. Compared with retinal isomers, the obvious advantage of stilbenes is that there is only one double bond in the stilbene isomers so they may be more suitable to be applied in our architecture in the future.

We have started with the investigation of trans- and cis- stilbenes (Fig.8,9). The excited states (singlets and triplets) of cis- and trans- stilbenes are calculated with both Single Configuration Interaction (CIS) method and Time Dependent Density Functional Theory (TDDFT). The lowest allowable excited states of both isomers are singlets. The wavelength of the first singlet excited states is in the UV region. The relatively large difference (267 meV with CIS, 100 meV with TDDFT) of excitation energies of the first singlet states of cis-stilbene and trans-stilbene makes stilbene idea attractive to achieve optically controllable directional transitions: cis-to-trans isomerization or trans-to-cis isomerization.

The infrared spectra of cis- and trans- stilbenes have been calculated with B3LYP/6-31G(d) method in G03W package (Fig.10). Although the distinguishable difference exists in vibrational spectra, there are no vibrations in the region below 30 cm⁻¹ that are of the most interest for us. Although THz spectra do not exist in cis- and trans- stilbenes, they do exist in derivatives of stilbenes. Most of stilbenes absorb in the UV region and will absorb in the visible region by introducing polar substituents as electron delocalizing groups into the stilbene structures.
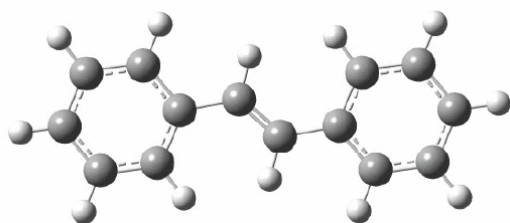
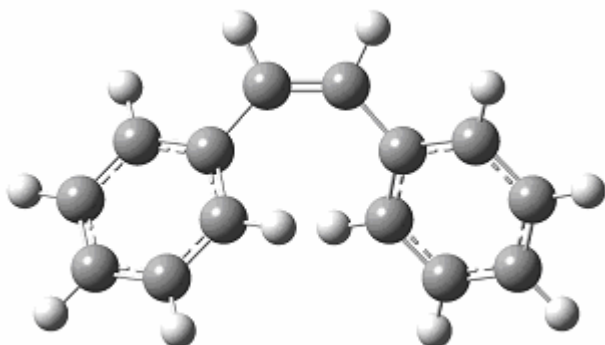Figure 8. Geometric structure of trans-stilbene



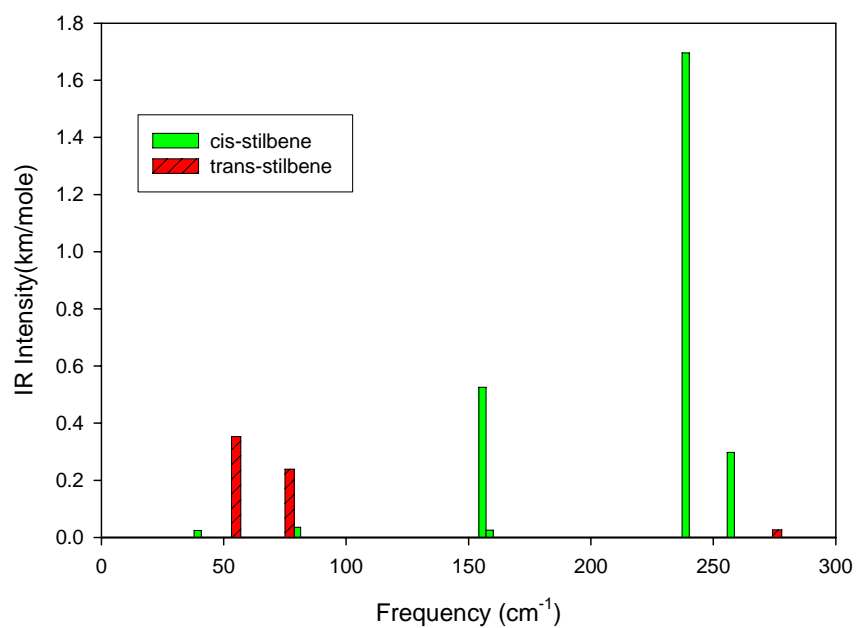Figure 9. Geometric structure of cis-stilbene.



Figure 10. Far infrared spectra of cis-stilbene and trans-stilbene ($<300$ cm$^{-1}$) calculated with B3LYP/6-31G(d) method in G03W and frequencies are scaled by 0.9603 to eliminate known systematic error.
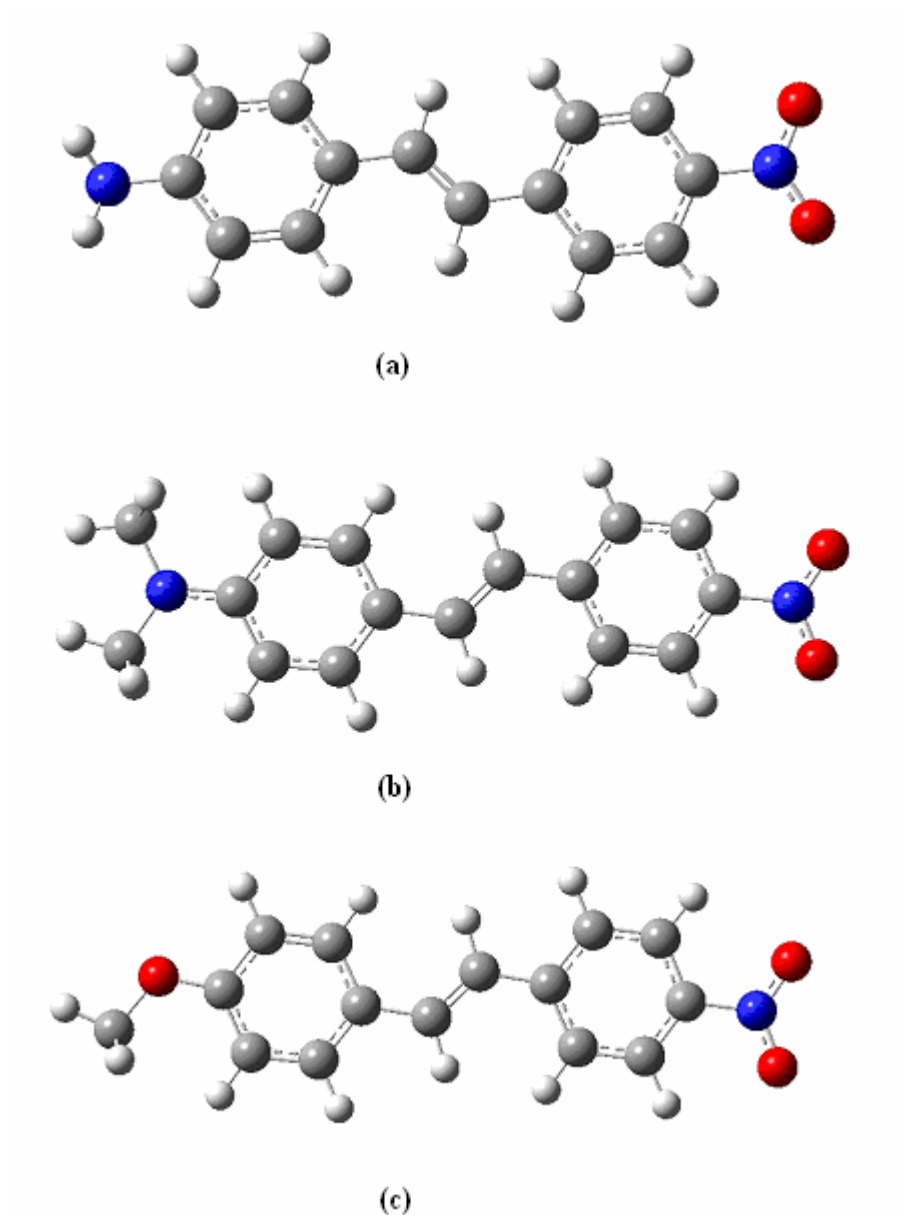
Figure 11. Geometric structures of some derivatives of stilbene: (a) 4-amino-4'-nitrostilbene; (b) 4-dimethylamino-4'-nitrostilbene; (c) 4-methoxy-4'-nitrostilbene

Some of derivatives we have investigated are are 4-amino-4'-nitrostilbene, 4-dimethylamino-4'-nitrostilbene, and 4-methoxy-4'-nitrostilbene (Fig.11).
The infrared spectra of cis- and trans- stilbenes derivatives have been calculated with B3LYP/6-31G(d) method in Gaussian03W. From our calculations , we can conclude that THz spectra exist in derivatives although they do not exist in stilbenes., The excited states (singlets) of various stilbene derivatives are calculated with Time Dependent Density Functional Theory (TDDFT). The lowest allowable excited

states have been shifted greatly to longer wavelength (Fig.15). The differences in the excitation energies of the first excited singlet states of cis- and trans- are big enough to be used to trigger directional photoisomerizations of trans- and cis- stilbene derivatives with different light sources.
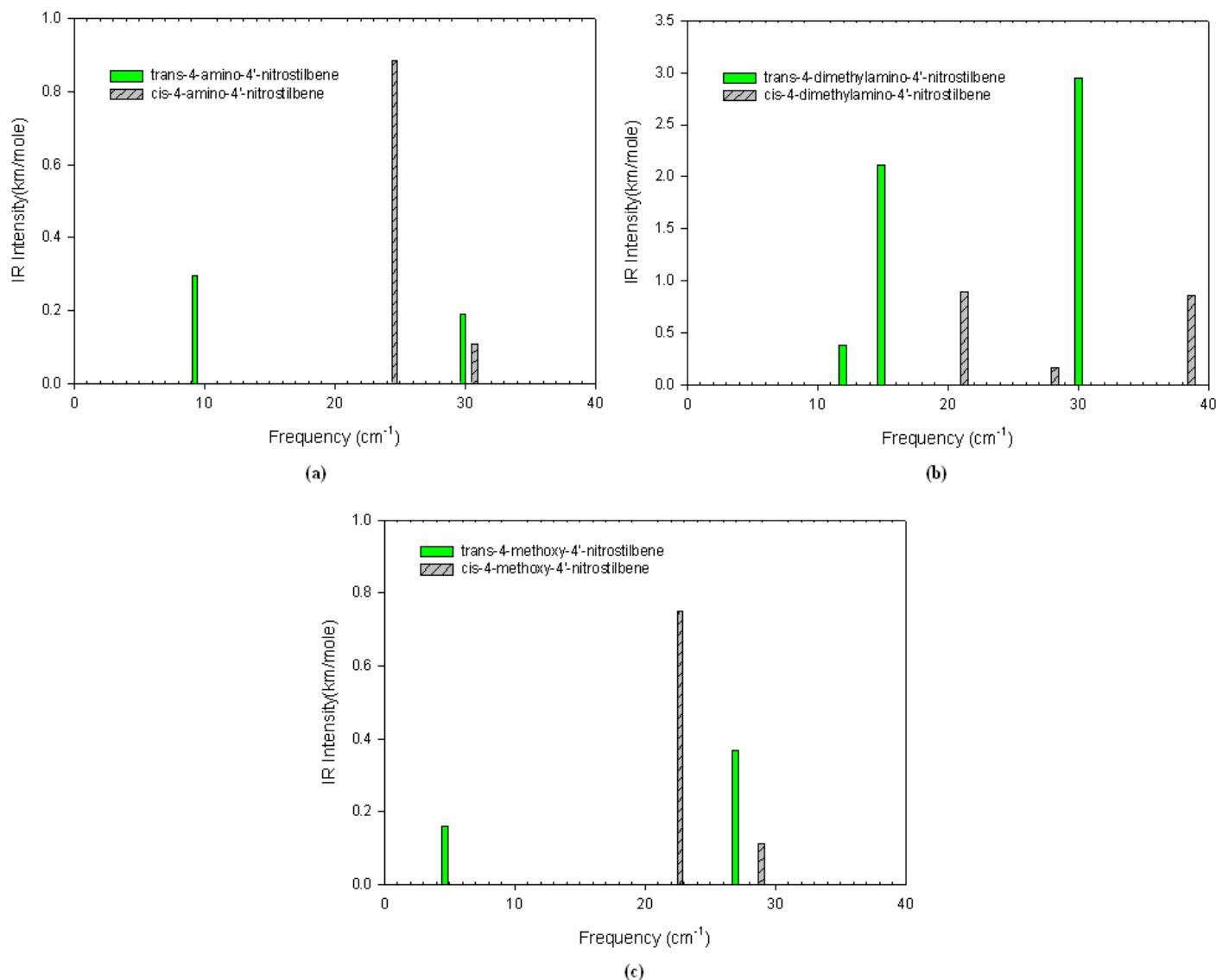


Figure 16. Very Far infrared spectrum of stilbene derivatives (<30 cm$^{-1}$) calculated with B3LYP/6-31G(d) method in G03W and frequencies are scaled by 0.9603 to eliminate known systematic error: (a) 4-amino-4'-nitrostilbene; (b) 4-dimethylamino-4'-nitrostilbene; (c) 4-methoxy-4'-nitrostilbene.

Prof. M. Norton has begun investigation of trimethoxystilbene capping as the possible binding of stilbene or its derivatives to DNA terminal. We have made proper simulations.
As the first step we have found the vibrational spectra of trimethoxystilbene carboxamide (TMS) (Fig.17) both for trans-and cis- isomers (Fig. 18). We can conclude from our calculations that THz spectra exist in TMS for both isomers. There is a big difference in frequencies of isomers . We studied the possible binding of stilbene or its derivatives to DNA terminal. Although the exposed terminal base pairs of DNA duplexes are nonclassical binding sites for small molecules, certain stilbenes can show capping when

14

tethered to the termini. Two optimized structures of trimethoxystilbene carboxamides that are 5'-tethered to one DNA base T with a complementary base A (TMS-TA) have been obtained, which means that two or more conformations are available for stilbene-DNA conjugates. The TMS molecule, which is almost parallel to the DNA base pair (T-A), is more stable than the almost vertical structure. We have also studied the excitation energies and the THz spectra of these two TMS-AT conformations.
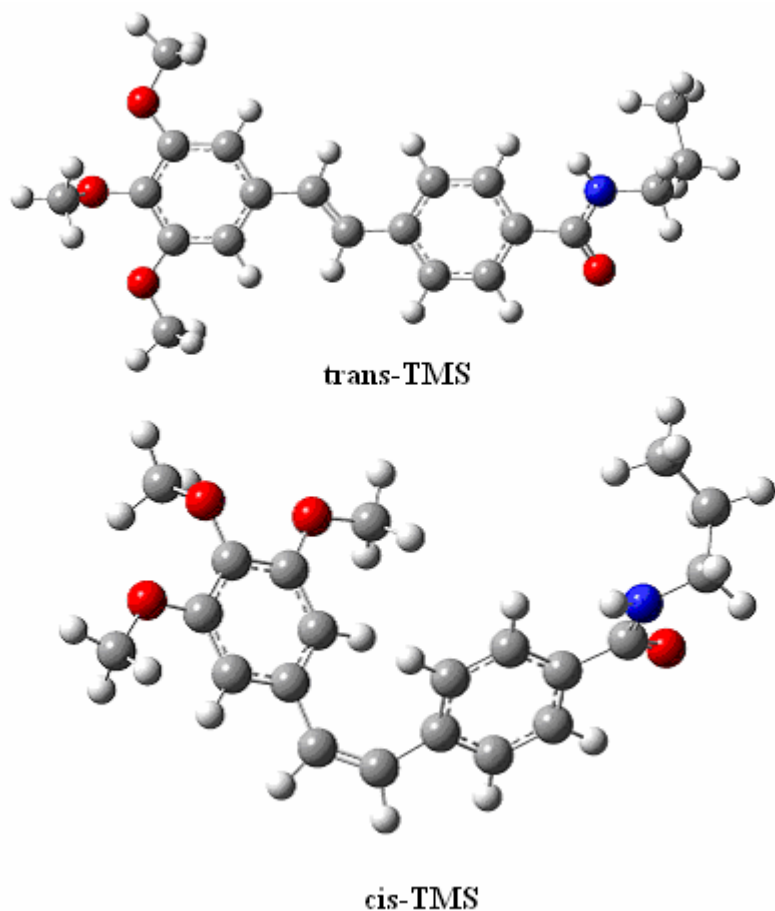


trans-TMS

cis-TMS

Figure 17. Geometric structure of trans- and cis- TMS
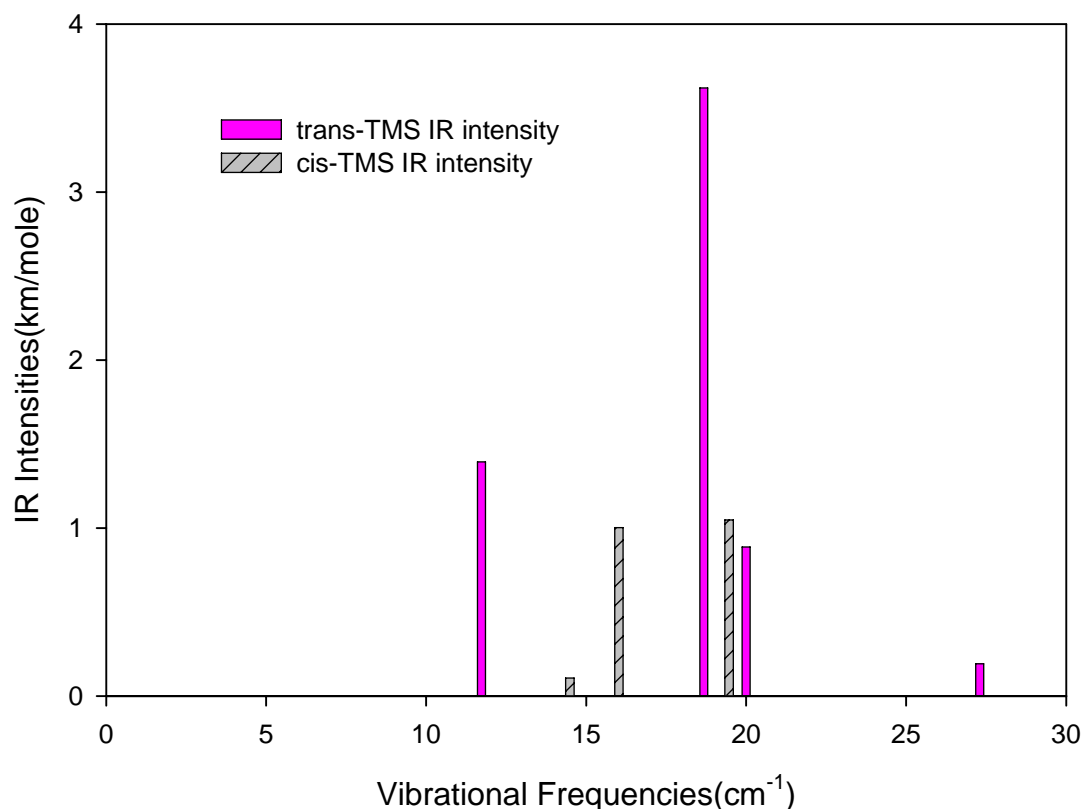
## trans- and cis- TMS



Figure 11. Vibrational spectra of trans- and cis- TMS in very far infrared region with frequencies scaled by 0.9603 to eliminate the systematic errors.


**Modeling of protonated DNA conjugates**

We analyzed the effect of basis set on optimization (conformation) results for DNA conjugate with TMS. In this simulations, we studied a protonated form of DNA base pair using Hartree-Fock. In low pH environment, this form is expected to be the most stable. In this study, we performed an optimization of protonated TMS – DNA with HF/6-31G* using Gaussian 98 and HF/sto-3g using G03W. The energy is substantially lower for the bigger basis set (6-31G*) as expected. The calculated dipole moment with HF/6-31G* is somewhat lower (9.94 Debye) than the dipole moment with HF/sto-3g (11.71 Debye). Different types of conformations for the T-A DNA with TMS derivative of stilbene can be classified as "open" and "closed". The optimization with HF/6-31G* was performed using the results from HF/sto-3g as an initial structure. However, the HF/sto-3g optimization started from the "closed" conformation. So within HF approximation, an "open" conformation seem to be rather stable. It is interesting to compare this result with the result obtained with HF/3-21G. This intermediate basis set optimization started from the "closed" conformation and it stayed "closed" as a result of the optimization. The optimized structures diverge from trans TMS form mainly due to a rotation over the C-C bond.

As the next step we studied in more detail a "closed" conformation (with TMS roughly parallel to the base pair plane) for the protonated T-A DNA conjugate. We started from our

16

optimization result for "closed" conformation generated with HF/3-21g We analyzed the stability of this conformation by increasing the basis set to 6-31g(d) and performing the structure optimization with HF/6-31g(d) using HF/3-21G result as a new starting structure. The structure has maintained a variant of a "closed" conformation, though it is not identical to the HF/3-21g result. In particular, the minimal distance between the end of TMS and the sugar has increased from ~2.5 angstrom to 2.9 angstrom. Throughout optimizations, TMS has essentially maintained "trans" conformation in conjugated state, but its two carbon rings are not in the same plane. Two substantially different conformations with HF/6-31g(d), "closed" and "open" are obtained. The "open" conformation has the total energy slightly (~0.02 eV) lower (less than $k_BT$ at room temperature). Its dipole moment is almost twice as big as the dipole moment of the "closed" conformation. Therefore, both "closed" and "open" conformations of TMS-TA were predicted with HF/6-31g(d). In simulated molecules, TMS itself maintains in the conjugated state a structure that corresponds to a twisted "trans" conformation. It is a "closed" conformation with the smallest distance between TMS and DNA ~ 2.1 angstrom.

The results for the electronic ground state of the same structure studied also with B3LYP. This density functional theory (DFT) approach is more suitable to describe gas phase molecules in the ground electronic states. Our DFT results confirm that both "open" and "closed" conformations might exist. The "open" structure is demonstrated obtained with b3lyp/3-21g and the "closed" structure is generated with b3lyp/3-21g*. The difference in basis sets is small (697 basis functions with 1146 primitive Gaussians for 3-21g* vs. 691 basis functions with 1140 primitive Gaussians for 3-21g), so we can roughly compare the obtained energies and frequencies. The difference in energy is approximately 5.5 eV or about $2k_BT$ per atom with "closed" form being the lower in energy. Also, the dipole moment of the "open" form is almost 1.5 times bigger. Hence, DFT results confirm that "open" form is more polarized. With HF/6-31g*, the predicted dipole moment for "open" form is ~5/3 bigger than for "closed" form. We are studying if a lower energy "open" form might exist. Hartree -Fock results obtained with 6-31g*, "open" and "closed" conformations are much closer in energy (within $k_BT$ at room temperature).

The frequencies and absorption intensities have been calculated. There are differences in position of peaks and intensities for "open" and "closed" forms, so the spectra are well distinguished. At lower end of the spectrum (especially below 30 cm$^{-1}$), higher accuracy computation might be needed to ensure reliable results.

### Modeling of DNA Conjugates: The Effect of Salt.

In low pH environment, a protonated DNA is expected to be the most stable. However, at normal pH, a DNA will be neutralized by a salt rather than by protons. We conducted an initial study of a sodium salt of TMS conjugate of a T-A DNA fragment. We performed an optimization of TMS – DNA salt using Gaussian 98 and HF/3-21G. The calculated the dipole moment of the salt form is more than twice bigger (19.64 Debye) than the dipole moment of the protonated form (9.45 Debye).

## 1.4 Conclusions

This first part of the report has presented a new bio-molecular electronic architecture that offers an enhanced capability for sensing THz-frequency bio-signatures. The studies presented in this report analyzed compound molecules of the type needed for realizing functional bio-molecular devices and derived their THz spectra and photo-induced methods for controlling the THz-frequency characteristics through changes to energy state and conformation. One possible fabrication approach for the construction of retinal-based two-dimensional nanostructures was also presented. We also initiated the investigation optimized structures of stilbene or its derivatives binding to DNA base pair to future application of stilbene-based device using DNA as scaffold. Two optimized structures are achieved where one of them is more restricted and the other is more flexible.

Future theoretical work will consider such functional bio-molecules that are bonded to traditional nano-scale semiconductor systems. The ultimate goal of this research is to define functioning bio-molecular devices (e.g., light guiding structures) that can be used to achieve bio-signature sensing and data processing in ultra-small integrated platforms.

## Laser Induced Millimeter Wave Fluorescence From Bio-materials

In recent years, the field of Terahertz (THz) science and technology has entered a phase of unprecedented expansion [3] and one of the major motivations for this renewed interest is the possibility of using THz spectral information for defense and security applications. For example, the very far-infrared region of the DNA absorption spectra, 3-100 cm-1 (or 0.1-3 THz), has been shown to reflect the low frequency molecular internal motions. In this range, the spectral features from bio-polymer molecules arise out of poorly localized low-frequency molecular internal vibrations such as twisting, bending and stretching of the double helix, sugar pseudo-rotational vibrations and fluctuations of weakest bonds or non-bonded interactions (van der Waals forces, dispersion forces, and hydrogen bonding). The internal motions, dependent on the weak hydrogen bonds of the double-helix base-pairs, are extremely sensitive to DNA composition and topology and have an impact on the main processes related to the transfer of genetic information, such as replication, transcription and viral infection. Hence, phonon modes that arise in this range can reflect features specific to the DNA code. In addition, theoretical studies have predicted the occurrence of DNA phonon frequencies throughout this region and many have been linked directly to experimental data. Therefore, the continued investigation of the far-infrared region of the DNA absorption spectra for the purpose of identifying DNA low-frequency internal motions are direct ways to obtain information about the peculiarities of DNA topology and internal motion. Furthermore, THz spectroscopy coupled with theoretical prediction can become a powerful tool for the investigation of the DNA structure and possible biological function.

In fact, a continuous and focused effort on THz sensing phenomenology in DNA and related biological materials [1, 4] was used to produce credible experimental evidence for the existence of species-specific resonance features that arise from phonon mode activity at the molecular

level. These demonstrations are important because they validate earlier theoretical predictions of a link between THz resonances and internal structure (e.g., dependent on hydrogen bonds of the double-helix base-pairs), and therefore defined a spectroscopic approach for interrogating microscopic information (e.g., genetic information encoded in the variety and arrangement of DNA nucleotides) that could be useful for bio-agent detection and analysis. Fourier transform (FT) transmission (absorption) spectroscopy has provided to this point the most detailed information on THz vibrational spectral signatures of biological molecules. While measurement of these THz spectral signatures is very difficult due to their relatively weak strength, there has been independently confirmation under varying laboratory conditions [5], and system-level studies [6-8], and there has even been theoretical predictions that these same THz-signatures are viable for use in medium-range remote-detection of bio-particles. Hence, this research clearly suggests potential payoffs for THz sensing and imaging in the biological and medical sciences and in other closely related military applications

Although numerous difficulties make the direct identification of THz phonon modes in biological materials very challenging, THz vibrational spectroscopy has demonstrated [8] that such measurements can be effective and fruitful. Spectra of different DNA samples reveal a large number of modes and a modest level of sequence-specific uniqueness. These internal motions are sensitive to DNA composition and topology, have an impact on the main processes related to the transfer of genetic information and eventually can give information regarding the three dimensional structure and flexibility of the DNA double helix. Hence, these prior successes motivate the investigations of new methodologies for the more efficient collection of long wavelength spectral information from biological materials and agents. As part of a joint project between the U.S. Army Edgewood Chemical Biological Center and the University of Virginia, a new approach to detecting and identifying DNA is being investigated that is based upon the premise that the DNA will radiate millimeter wave (MMW) and/or submillimeter wave (sub-MMW) energy upon the absorption of infrared (IR) radiation. The proposed hypothesis assumes that the excitation of molecular vibrations in the DNA by the application of laser energy, at known IR absorption peaks, can lead to the production of low frequency (MMW and/or THz) radiation from the DNA through nonlinear phonon-decay processes. If this hypothesis is valid, and there is certainly evidence to suggest that this could be possible as elemental units of DNA exhibit strong absorption in the IR, then the resulting long wavelength fluorescence should provide a much more effective methodology for probing the allowed vibrational modes associated with biological agents of interest.

This approach can be visualized as a far infrared fluorescence of biological molecules. The infrared radiation can excite the vibrational bonds. It is possible that vibrational relaxations may result in energy emission into lower (sub-millimeter and millimeter) spectral regions. This long wavelength fluorescence might be an alternative approach to bio-detection. The millimeter/sub-millimeter-wave frequency regime is expected to have multiple spectral features that are dependent on DNA internal vibrations. The vibrations are spread over large portions of the complex molecule. Thus, spectral emission dependent on the primary sequence of the molecule may be expected . The acquisition of millimeter/sub millimeter-wave spectroscopy is limited due to low absorption of THz radiation by the DNA molecule. Therefore, it is desirable to investigate non-THz region radiation absorption pathways that may result in THz region emission spectra. In other words, our plan is to look for "other than THz excitation source" to obtain emission spectra in THz region. In this work we conducted the initial theoretical investigation of emission of radiation by DNA upon the absorption of powerful infrared (IR) radiation. We studied the

anharmonicity of different transitions that are responsible for the vibrational energy transfer from IR region to lower frequencies. Fermi resonance is such an energy transition pathway. We performed the vibrational analyses of four different monophosphates including deoxycytidine 5'-monophosphate (dCMP), deoxythymidine 5'-monophosphate (dTMP), deoxyadenosine 5'-monophosphate (dAMP), and deoxyguanosine 5'-monophosphate (dGMP) within Hartree-Fock approximation and the density functional theory (DFT) in G03W package. Initially the IR absorption bands must be evaluated. Then, for each of the IR absorption band in 900 to 1100 cm$^{-1}$ wavenumber region, the probability of Fermi resonance must be estimated. If an IR absorption band indicates higher probability of energy transition via Fermi resonance, it indicates the possible occurrence of emission bands in the millimeter wave (MMW) region. An observable indicator of this transition is occurrence of emission band at twice the wavelength of excitation radiation. An IR spectroscope can be used to confirm the presence of the emission band. If the emission band is observed, THz emission spectra can be measured at MMW region. Figure 1 shows a flow chart that describes our approach.
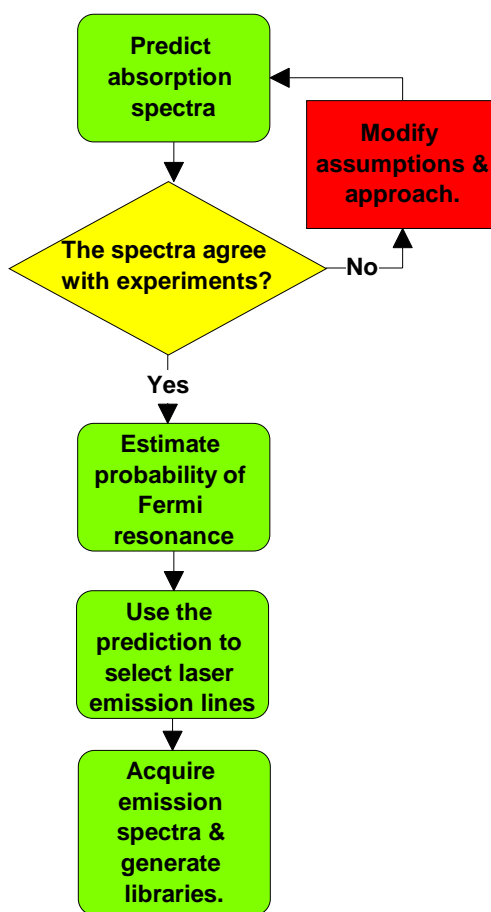


Figure 12 . Outline of our approach to obtaining THz region emission spectra from an IR excitation source.

## 2.1 Theoretical Vibrational Analyses

Long-wavelength vibrational absorption (transmission) spectra    may be used for detection of DNA molecule. The theoretical investigation of emission of millimeter/sub-millimeter waves (MMW) radiation by DNA upon the absorption of IR radiation is the objective of this study. The carbon dioxide ($CO_2$) laser will be the candidate for the source of IR radiation, thus the frequencies in the region between 9 microns and 11 microns are of interest. The output of a $CO_2$ laser is medium-IR radiation around a range near 10.6 microns. Therefore possible light induced transitions have to be found at this wavelength. These transitions are related to the bond vibrations including only small group of atoms. Hence it is possible to analyze different fragments of DNA for identification of possible transitions to MMW region upon the absorption of IR radiation. Therefore, the newly proposed approach requires a comprehensive theoretical analysis of the vibrational modes and interactions within the DNA molecular structure, as applied to millimeter wave emission. Such an analysis starts from development a theoretical model.  We have begun with analyses of IR absorption by nitrogenous bases and then we studied absorption of monophosphates as it is known the single stranded DNA consists of nucleotides connected with each other via phosphates groups. We performed the vibrational analyses of four different monophosphates including deoxycytidine 5'-monophosphate (dCMP), deoxythymidine 5'-monophosphate (dTMP), deoxyadenosine 5'-monophosphate (dAMP), and deoxyguanosine 5'-monophosphate (dGMP) within Hartree-Fock approximation and the density functional theory (DFT) in G03W [2] package to estimate the absorption bands in the IR spectral region. The transfer absorbed IR energy is the key process for emission in MMW region. The proposed theoretical model considers the molecule of interest as a system of coupled oscillators. The emission is expected due to the energy transfer from one excited oscillator to another with lower frequency. Strong coupling is required for this process. Therefore, we study the anharmonicity of different transitions that are responsible for the vibrational energy transfer from IR region to lower frequencies.

### Fermi Resonance

Difficult part of the theoretical study is the analysis of the possible channels for transferring the energy associated with the IR excitation to the lower-energy (i.e., longer wavelength) vibrations. Anharmonicity is the cause of coupling of two nearly identical frequency (one of which is the excitation radiation) oscillators in complex molecules. The result of such coupling is the Fermi resonance, which may result in transfer of absorbed energy via multiples of absorbed excitation radiation wavelength.  If the vibrational frequency coincides with the frequency of the laser radiation transition from the ground state to the first excited level of the oscillator occurs under influence of the laser radiation. Such a picture is valid for harmonic oscillators when only the parabolic potential is taken into account. Normal mode analysis of standard algorithms gives us possibility to find all available oscillator frequencies and to calculate probabilities of any transition. The selection rule for a harmonic oscillator states that transitions are allowable only between adjacent levels of the same oscillator. All transitions between different oscillators are forbidden. However the vibrations of real molecules are not strictly harmonic and the oscillators are coupled because of the anharmonicity. The potential is parabolic only in the lowest order of expansion into displacements of atoms. The anharmonicity is responsible for coupling of the oscillators and the energy transfer. We study a rather complex molecule with many atoms. The

potential is a function of 3N-6 variables where N is the number of atoms. In order to estimate the possible effect of nonparabolicity on oscillator coupling some relatively simple approach has to be developed. In the lowest order of the expansion in the atomic displacements, δr, the nonparabolic part of the potential of the interaction between two atoms, $v_{np}$, is proportional to the third power of the displacements.

$$v_{np}(1,2) = (\frac{\partial^3 V}{\partial r^3})_0 \frac{((\delta\vec{r}(1) - \delta\vec{r}(2))(\vec{r}_0(1) - \vec{r}_0(2)))^3}{6|\vec{r}_0(1) - \vec{r}_0(2)|^3} \tag{1}$$

We have taken into account only stretching of the bond. Hence only relative displacement of atoms is important. According to our approximation the total nonparabolic potential includes only interaction between nearest neighbors

$$V_{np} = \frac{1}{2}\sum_{k,l} v(k,l) \tag{2}$$

Such terms can be responsible for the coupling between the first excited state of one oscillator, which is populated as a result of the laser radiation, and the second excited states of the other oscillator. If the energy of these two states is close enough the Fermi resonance occurs. The displacement of atomic coordinates is connected with eigenvectors of oscillators in the following way

$$\delta\vec{r}(k)\sqrt{M_k} = \sum_j \vec{s}(k\,|\,j)q_j \tag{3}$$

where $\vec{s}$ is Eigen vectors of oscillator j, qs are normal coordinates, $M_k$ is the atomic mass.
The matrix element of the nonparabolic potential between two states of two oscillators, j and n, can be written as follows:

$$< j1; n0\,|\,V_{np}\,|\,j0; n2 >= \frac{1}{4\omega_n\omega_j^{1/2}\,|\vec{r}_0(1) - \vec{r}_0(2)|^3}(\frac{\partial^3 V}{\partial r^3})_0$$

$$((\frac{\vec{s}(1\,|\,j)}{M_1^{1/2}} - \frac{\vec{s}(2\,|\,j)}{M_2^{1/2}})(\vec{r}_0(1) - \vec{r}_0(2)))((\frac{\vec{s}(1\,|\,n)}{M_1^{1/2}} - \frac{\vec{s}(2\,|\,n)}{M_2^{1/2}})(\vec{r}_0(1) - \vec{r}_0(2)))^2 \tag{4}$$

At first we estimated the coupling of the oscillators using the first order of the perturbation theory. However it proved that some oscillators are strongly coupled. In this case we have taken into account an interaction only between these two oscillators. The energies of two coupled are renormalized

$$E_1 = [E(j1; n0) + E(j0; n2)]/2 + \Delta/2 \tag{5a}$$
$$E_2 = [E(j1; n0) + E(j0; n2)]/2 - \Delta/2 \tag{5b}$$

Energy level splitting of two renormalized levels $\Delta$ is as follows

$$\Delta = \{\delta^2 + 4 \mid < j1; n0 \mid V_{np} \mid j0; n >\mid^2\}^{1/2} \tag{6}$$

Splitting of unperturbed levels $\delta$ is determined by

$$\delta = \mid E(j1; n0) - E(j0; n2) \mid \tag{7}$$

The wave functions of two resulting states are

$$\psi_1 = a \mid j1; n0 > -b \mid j0; n2 > \tag{8a}$$

$$\psi_2 = b \mid j1; n0 > +a \mid j0; n2 > \tag{8b}$$

where

$$a = (\frac{\Delta + \delta}{2\Delta})^{1/2} \tag{9a}$$

$$b = (\frac{\Delta - \delta}{2\Delta})^{1/2} \tag{9b}$$

As a result the transition occurs between the $\mid j1; n0 >$ state of the oscillator j and $\mid j0; n2 >$ state of the oscillator n. The probability is proportional to $\mid b \mid^2$. The spontaneous emission from $\mid j0; n2 >$ state of the oscillator n to the first excited state and then to the ground state becomes possible and such fluorescence can be detected. Figure 2 shows a graphical representation of Fermi resonance.
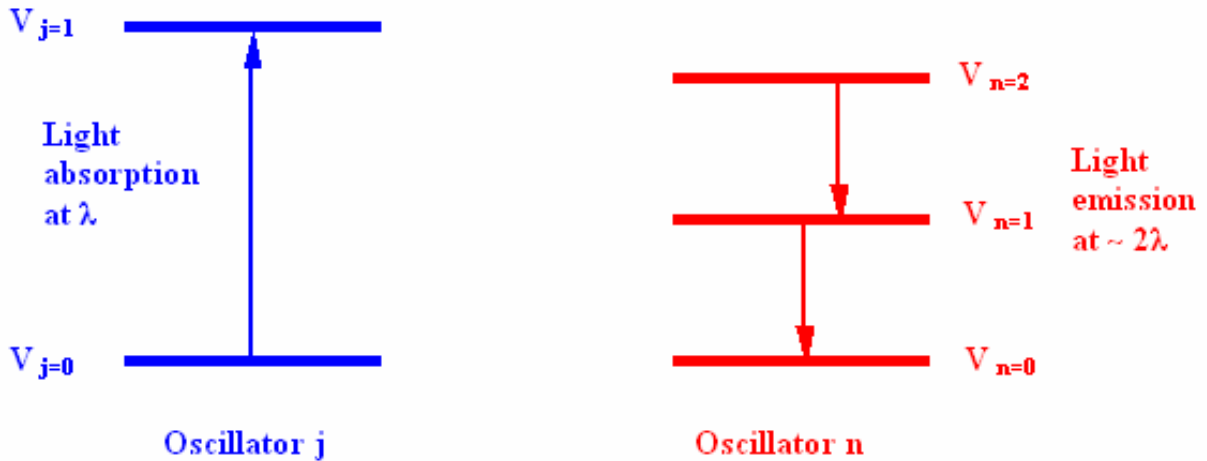


Figure 13. Fermi resonance is a splitting of lines in an infrared spectrum. It occurs when two vibrational states of a molecule have different modes of movement but almost the same energy.

## 2.2 Experimental

The laser excitation source along with power attenuating and continuous-to-pulsed mode conversion optics was set-up. A continuous tune-able $CO_2$ laser serves as the excitation source. The laser is capable of emitting 80 emission lines in 9.6 and 11.4 μm wavelength range. The laser power is controlled by a combination of polarization based attenuators and a ZnSe optics based beam expander. The laser operates in continuous (CW) mode. The emission wavelength is measured with a $CO_2$ laser spectrum analyzer. Three $CO_2$ laser emission lines were used as the excitation source – at 970 cm$^{-1}$ (10.31 μm wavelength), at 1080 cm$^{-1}$ (9.26 μm wavelength) and at 949 cm$^{-1}$ wavenumber (10.54 μm wavelength). Transmission FTIR spectra were obtained while exposing the sample to these laser lines with a FTIR spectrometer coupled with a Deuterated tri-glycine sulfate (DTGS) pyroelectric detector . Figure 14 shows the experimental setup. Genetic components such as adenosine, guanosine, dAMP, dGMP, dCMP and Herring sperm DNA were dissolved or suspended at 20 mg/ml concentration in de-ionized water. A one milliliter aliquot of the prepared aqueous solution or suspension was coated on 1.5 inch diameter, 5 mm uncoated ZnSe window. Upon drying, a film residue of the dissolved or suspended chemical remained on the ZnSe window. FTIR spectra of the prepared chemicals samples were obtained with a SiC IR source .
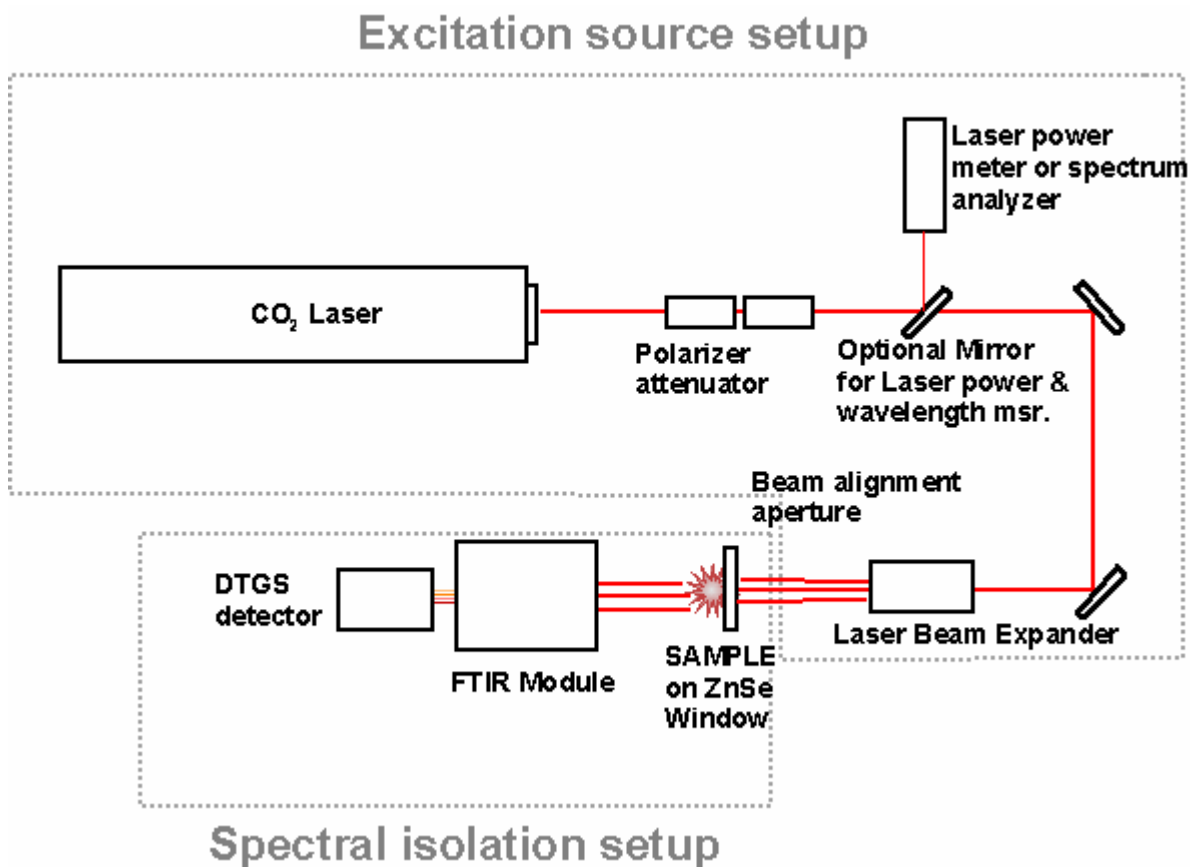


Figure 14. Experimental setup for spectral acquisition.

The sample on ZnSe window was exposed to the laser. The sample side of the ZnSe window faced the FTIR instrument. This is because, ZnSe is transparent to IR radiation up to 20 μm only. The CW mode of operation may result in thermal energy build up in the sample. Laser power density was optimized with the polarizer attenuators and beam expander to maximize FTIR signal strength without causing any thermal induced damage to the sample (Herring Sperm DNA). The lack of damage was ascertained by examining the FTIR spectra of the sample before and after the exposer to the laser. The FTIR spectra obtained before the exposer to CW laser matched with that obtained after the exposer to CW laser.

## 2.3 Results and Discussions

Fermi resonance modeling strongly suggests that a possibility of energy transfer to lower energy states exists. Thus, we conducted limited laser-excitation experiments. The samples coated on ZnSe windows were exposed to three different laser lines at 970 cm$^{-1}$ (10.31 μm wavelength), at 1080 cm$^{-1}$ (9.26 μm wavelength) and at 949 cm$^{-1}$ wavenumber (10.54 μm wavelength). A single spectrum was the result of 100 consecutive spectral co-adds for improved signal to noise ratio. Boxcar apodization technique was used to obtain the FTIR spectra. Figure 9-11 show the spectral response to the three laser lines. The region shaded in grey is the twice the incident radiation wavelength region. A small emission line (no more than 2 % of the incident laser line intensity) at twice the wavelength was observed for most of the DNA components. Figure 15 shows strong emission peak at twice the wavelength (540 cm$^{-1}$ wavenumber ) for polystyrene, guanosine and adenosine when excited with 1080 cm$^{-1}$ laser line . Where as, Figure 16 shows strong emission peak at twice the wavelength (485 cm$^{-1}$ wavenumber ) for guanosine , adenosine and dGMP when excited with 970 cm$^{-1}$ laser line. Figure 17 shows emission peak at twice the wavelength (474 cm$^{-1}$ wavenumber ) for DNA , adenosine and dGMP. Also a very strong emission peak for guanosine is observed at 474 cm$^{-1}$ wavenumber when excited with 970 cm$^{-1}$ laser line. Figure 182 shows the cumulative emissive spectral response from exposer to the three laser lines. The grey region shows the twice the incident radiation wavelength region. Clearly response from each of the sample is visually different from each other. This finding may indicate occurrence of Fermi resonance, which needs to be confirmed with computational modeling.
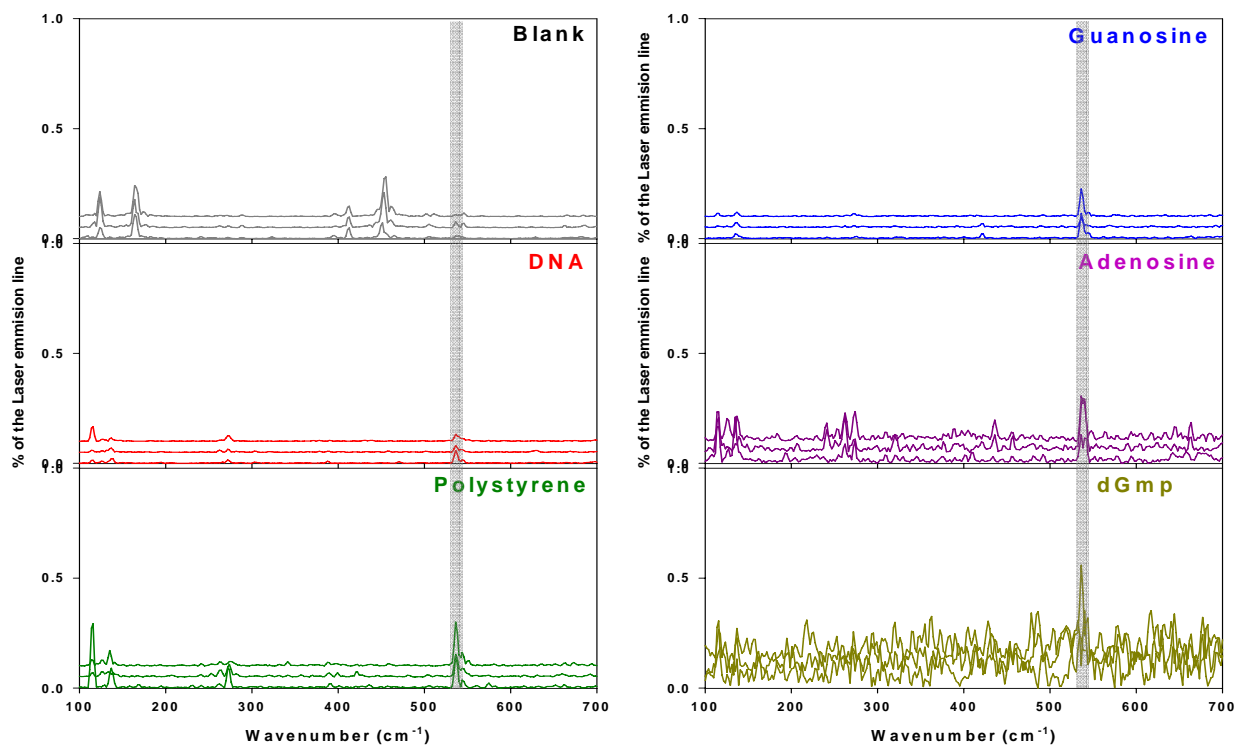
Figure 15. Emission / Transmission spectra when excited by 1080 cm$^{-1}$ CO$_2$ laser line. Each spectrum is average of 100 spectra.
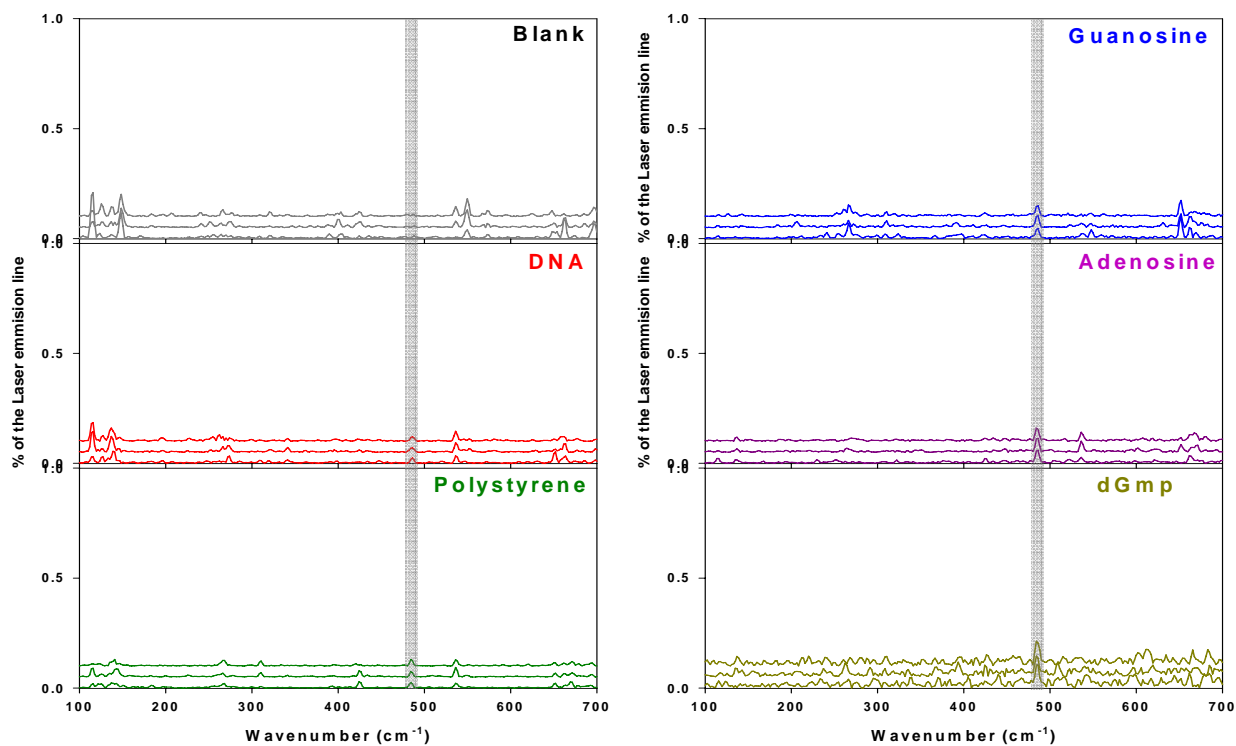
Figure 16. Emission / Transmission spectra when excited by 970 cm$^{-1}$ CO$_2$ laser line. Each spectrum is average of 100 spectra.
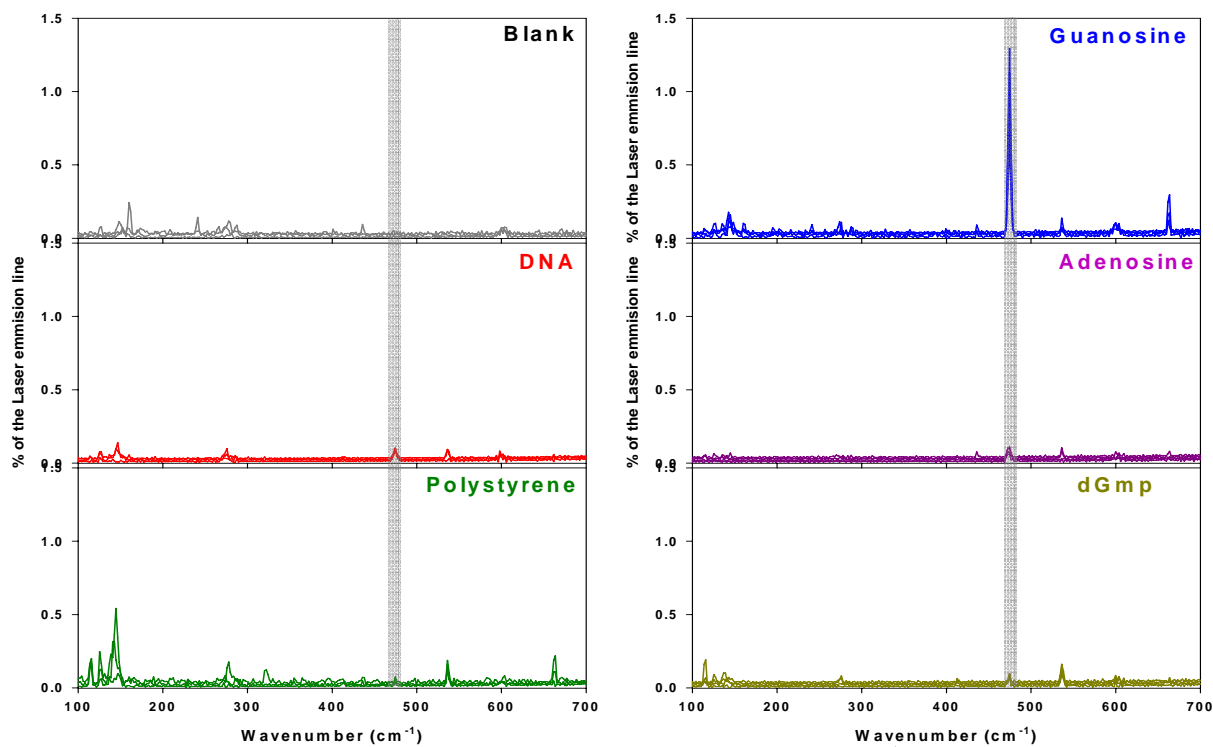


Figure 17. Emission / Transmission spectra when excited by 949 cm$^{-1}$ CO$_2$ laser line. Each spectrum is average of 100 spectra.
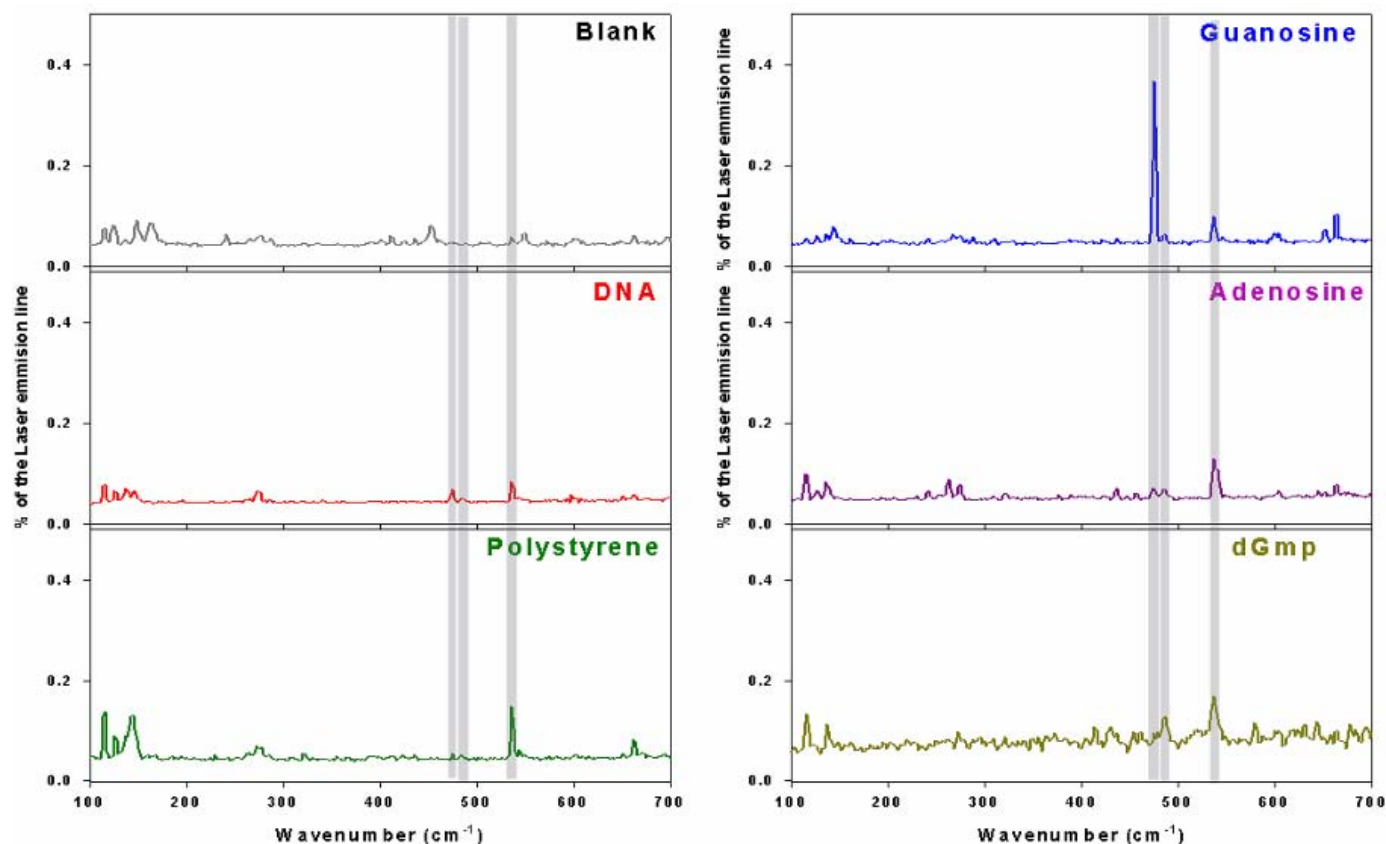
Figure 18 . Estimated Emission / Transmission spectra when excited by a scanning.

## 2.3 Conclusions

From the viewpoint of the quantum mechanics a mixing of two states of two oscillators occurs with large probability. Hence the Fermi resonance provides a channel for a most effective transfer of energy. In our simulation we identify numerous Fermi resonances in the region of our interest. Different transitions in DNA monophosphates including dAMP, dCMP, dGMP and dTMP caused by anharmonicity transitions have been analyzed. The probabilities of transitions have been calculated and the most effective channels of the energy transfer have been identified. The most important prediction of our research was as the first step to study the emission in the region of wave length of the order 20 μm which is twice larger than the wave length of the $CO_2$ laser operation .

In our experiment we have detected a small emission line (no more than 2 % of the incident laser line intensity) at twice the wavelength for most of the DNA components. This finding may indicate occurrence of Fermi resonance. Therefore, these findings suggest that upon strong absorption of infrared radiation, DNA will radiate MMW and/or SubMMW energy.

We recommend further investigation in modeling and experimental conformation of DNA absorption spectra and emission spectra at near MMW/SubMMW region.

# References

[1]  T. Globus, D.Woolard, M. Bykhovskaia,  B. Gelmont,  L. Werbos, A. Samuels,  **"** THz-Frequency  Spectroscopic Sensing of DNA and Related Biological Materials **",** pp.1-34**,** *Terahertz Sensing Technology*, v.2, ed. D. Woolard, M. Shur, and W. Loerop , World Scientific, 2003.

[2] M. J. Frisch, et. al., "Gaussion Software Package" Gaussian, Inc., Pittsburgh, PA (2002).

[3] D. Woolard, E. Brown, M. Pepper, M. Kemp, IEEE Proc., 2005.

[4] D. L. Woolard, T. R. Globus, B. L. Gelmont, M. Bykhovskaia, A. C. Samuels, D. Cookmeyer, J. L. Hesler, T. W. Crowe, J. O. Jensen, J. L. Jensen, and W.R. Loerop,  " Submillimeter-Wave Phonon Modes in DNA Macromolecules", Phys. Rev E. v.65,  pp. 1903-1914, 2002

[5] E. R. Brown, J. E. Bjarnason, T. L. J. Chan, A. W. M Lee and M. A. Celis, Applied Physics Letters, 84, p 3438-3440, 2004.

[6] D. L. Woolard, E. R. Brown, et.al. IEEE MTT-S Int. Microwave Symp. Dig., Philadelphia, PA, June 8-13, 2003, pp. 763-766.

[7] E. R. Brown, D. L. Woolard, et. al. Proc. Int. Microwave Symp., Seattle, WA, June 2-6, 2002.

[8]  D. Woolard, E. Brown, A. Samuels, T. Globus, B. Gelmont, and M.Wolski , "Terahertz-frequency Spectroscopy as a  Technique for the Remote Detection of Biological Warfare Agents",  in Proceedings to the 23nd Army Science Conference, Orlando, Florida, Dec.2-5,2002