TERAHERTZ SPECTROSCOPY AND LASER INDUCED INFRARED EMISSION SPECTROSCOPY OF NITROMETHANE

AND

OPTICAL PROPERTIES OF LASER-INDUCED CARRIERS ON SEMICONDUCTOR SURFACES PROBED BY A 10.6 μm WAVELENGTH CO₂ LASER

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Abstract

This work consists of two parts, (1) Terahertz (THz) spectroscopy and laser-induced infrared emission spectroscopy of nitromethane and (2) optical properties of laser-induced carriers on semiconductor surfaces probed by a 10.6 μm wavelength CO₂ laser. In the spectroscopic study of nitromethane, previously unreported low resolution rotational-torsional spectra in the THz frequency were obtained by a Bruker IFS 66 v/S Fourier transform spectrometer. The acquired spectra were then compared with a calculation based on a rotational-torsional Hamiltonian which includes centrifugal distortions and rotational-torsional coupling terms. Even though the constants used in the calculation were a result of fitting the microwave spectrum, a discrepancy was observed between the calculated and the experimentally obtained spectrum.

In addition, gaseous nitromethane was irradiated with a c.w. CO₂ laser (~ 20 W cm⁻² intensity, 10.6 μm wavelength) and the laser-induced steady state emission spectrum was analyzed with the IFS 66 v/S spectrometer. The laser-induced emission spectrum showed the characteristics consistent with the laser-heated thermal emission. The decay constant of the emission followed by a 100 ms CO₂ laser pulse was measured with a pyroelectric detector and determined to be 0.3 s.

In part II, several polycrystalline semiconductors [silicon (Si), germanium (Ge), gallium arsenide (GaAs), and cadmium telluride (CdTe)] were irradiated with a 150 ps Nd:YAG laser (532/1064 nm wavelength) and induced changes in the optical properties were monitored by measuring the time-resolved reflectance and transmittance of a low power CO₂ laser incident on the samples at the Brewster angle. The experimental results showed a sub-nanosecond increase in the reflectance and a longer increase in the
absorption as a result of electron-hole pairs \((i.e.\) carriers) generated by absorption of the incident Nd:YAG laser pulses.
# TABLE OF CONTENTS

Acknowledgements ............................................................................................... iv
Abstract .................................................................................................................. v
List of Tables .......................................................................................................... viii
List of Figures ......................................................................................................... ix

**PART I THz spectroscopy and laser induced infrared emission spectroscopy of nitromethane**

Chapter 1: Introduction .......................................................................................... 2
Chapter 2: Molecular Hamiltonian and absorption coefficients Review
  2.1 Rotational and vibrational Hamiltonian ......................................................... 9
  2.2 Radiation interaction .................................................................................... 19
  2.3 Absorption coefficient .................................................................................. 23
Chapter 3: Rotational-torsional levels and absorption coefficients of CH₃NO₂
  3.1 Rotational-torsional levels .......................................................................... 26
  3.2 Electric dipole transition moments and absorption coefficient ................. 30
  3.3 Laser induced IR emission spectrum of CH₃NO₂ ....................................... 34
Chapter 4: Experiment
  4.1 Fourier Transform Spectrometer (FTIR) ....................................................... 36
  4.2 Experiment Setup (THz spectrum of CH₃NO₂) ............................................. 41
  4.3 Experiment Setup (laser induced IR emission of CH₃NO₂) ....................... 42
Chapter 5: Results and discussion
  5.1 THz spectrum of CH₃NO₂ ............................................................................ 49
  5.2 CO₂ laser induced IR emission spectrum .................................................... 54

**PART II Optical properties of laser-induced carriers on semiconductor surfaces probed by a 10.6 μm CO₂ laser**

Chapter 6: Introduction ........................................................................................ 63
Chapter 7: Laser-induced carrier dynamics of a semiconductor
  7.1 Carrier dynamic ............................................................................................ 68
  7.2 Reflectance and transmittance .................................................................... 73
Chapter 8: Experiment .......................................................................................... 76
Chapter 9: Results and discussion
  9.1 Si .................................................................................................................. 81
  9.2 Ge ................................................................................................................ 88
  9.3 GaAs and CdTe ........................................................................................... 92
  9.4 Damage threshold ....................................................................................... 98
Chapter 10: Conclusion ......................................................................................... 99
Appendix ............................................................................................................... 105
Reference ............................................................................................................. 108
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-1 Rotational-torsional Hamiltonian parameters of CH$_3$NO$_2$</td>
<td>28</td>
</tr>
<tr>
<td>3-2 Equilibrium positions and effective charges of atoms in CH$_3$NO$_2$</td>
<td>33</td>
</tr>
<tr>
<td>4-1 Components/spectral ranges of the Bruker IFS 66v/S spectrometer</td>
<td>41</td>
</tr>
<tr>
<td>5-1 Coefficients appearing in EQ. (5-1)</td>
<td>53</td>
</tr>
<tr>
<td>9-1 Material properties of Si</td>
<td>83</td>
</tr>
<tr>
<td>9-2 Laser induced damage threshold</td>
<td>98</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figures</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1 The number of THz radiation related articles</td>
<td>3</td>
</tr>
<tr>
<td>1-2 Transmittance of common packing materials</td>
<td>5</td>
</tr>
<tr>
<td>2-1 Graphical description of electronic and rovibrational energy levels</td>
<td>13</td>
</tr>
<tr>
<td>2-2 Absorption spectrum of CO$_2$</td>
<td>22</td>
</tr>
<tr>
<td>2-3 Calculated absorption coefficients of oblate rotors in various sizes</td>
<td>25</td>
</tr>
<tr>
<td>3-1 Geometrical configuration of CH$_3$NO$_2$</td>
<td>26</td>
</tr>
<tr>
<td>4-1 Schematic representation of the Michelson interferometer</td>
<td>37</td>
</tr>
<tr>
<td>4-2 Bruker IFS 66v/S spectrometer</td>
<td>39</td>
</tr>
<tr>
<td>4-3 Schematic view of Bruker IFS 66v/S spectrometer</td>
<td>40</td>
</tr>
<tr>
<td>4-4 Source spectrum of FTIR under vacuum and vented</td>
<td>40</td>
</tr>
<tr>
<td>4-5 Setup used to acquire CO$_2$ laser induced IR emission spectrum of CH$_3$NO$_2$</td>
<td>43</td>
</tr>
<tr>
<td>4-6 Picture of the PL module</td>
<td>44</td>
</tr>
<tr>
<td>4-7 CO$_2$ laser flux measurement</td>
<td>45</td>
</tr>
<tr>
<td>4-8 Setup used to measure the decay constant of CO$_2$ laser induced IR emission</td>
<td>46</td>
</tr>
<tr>
<td>4-9 P4 pyroelectric detector's response function</td>
<td>48</td>
</tr>
<tr>
<td>5-1 Measured (black) and calculated (red) THz spectrum of CH$_3$NO$_2$</td>
<td>50</td>
</tr>
<tr>
<td>5-2 THz spectrum of CH$_3$NO$_2$ (top) and distilled water (bottom)</td>
<td>51</td>
</tr>
<tr>
<td>5-3 Calculated rotational-torsional transitions at 300K</td>
<td>51</td>
</tr>
<tr>
<td>5-4 C.W. CO$_2$ laser induced IR emission spectrum of CH$_3$NO$_2$</td>
<td>55</td>
</tr>
</tbody>
</table>
5-5 C.W. CO2 laser induced IR emission spectrum of CH₃NO₂, N₂ purged ............ 56
5-6 IR absorption spectrum of CH₃NO₂ .............................................................. 56
5-7 Pyroelectric detector output of the laser induced emission ......................... 59
5-8 Laser-induced IR emission at various pressures ......................................... 60
5-9 Emission intensities and decay constant of the laser-induced IR emission ....... 60
5-10 Low resolution laser-induced IR emission spectra of CH₃NO₂ ....................... 61
5-11 Laser-induced IR emission spectrum of CH₃NO₂ in atmosphere .................... 61
6-1 Schematic description of cavity dump mechanism .................................. 65
8-1 Schematic description of experiment setup .............................................. 77
8-2 Laser fluence calibration curve ............................................................... 78
8-3 Photoelectromagnetic (PEM) detector ...................................................... 78
8-4 Data acquisition and synchronization setup .............................................. 80
9-1 Time-resolved transmittance of Si irradiated at 532 nm wavelength ............ 83
9-2 Time-resolved transmittance of Si irradiated at 1064 nm wavelength .......... 84
9-3 Minimum transmittance of Si irradiated at 1064 nm and 532 nm wavelength ..... 84
9-4 Calculated integrated laser-induced carrier density of Si .......................... 85
9-5 Reflectance of Si surface irradiated at 532 nm wavelength ......................... 86
9-6 Peak reflectance of Si irradiated at 532 nm wavelength ............................. 87
9-7 Calculated surface carrier density of Si irradiated at 1064 nm and 532 nm ..... 87
9-8 Time-resolved transmittance of Ge irradiated at 532 nm wavelength .......... 88
9-9 Time-resolved transmittance of Ge irradiated at 1064 nm wavelength .......... 89
9-10 Minimum transmittance of Ge irradiated at 532 nm and 1064 nm wavelength .... 89
9-11 Reflectance of Ge irradiated at 1064 nm wavelength ............................... 90

x
<table>
<thead>
<tr>
<th>Page</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>9-12</td>
<td>Reflectance of Ge irradiated at 532 nm wavelength</td>
</tr>
<tr>
<td>9-13</td>
<td>Peak reflectance of Ge irradiated at 532 nm and 1064 nm wavelength</td>
</tr>
<tr>
<td>9-14</td>
<td>Time-resolved transmittance of GaAs irradiated at 532 nm wavelength</td>
</tr>
<tr>
<td>9-15</td>
<td>Time-resolved transmittance of GaAs irradiated at 1064 nm wavelength</td>
</tr>
<tr>
<td>9-16</td>
<td>Minimum transmittance of GaAs irradiated at 532 and 1064 nm wavelength</td>
</tr>
<tr>
<td>9-17</td>
<td>Time-resolved transmittance of CdTe irradiated at 532 nm wavelength</td>
</tr>
<tr>
<td>9-18</td>
<td>Time-resolved transmittance of CdTe irradiated at 1064 nm wavelength</td>
</tr>
<tr>
<td>9-19</td>
<td>Minimum transmittance of CdTe irradiated at 532 and 1064 nm wavelength</td>
</tr>
<tr>
<td>9-20</td>
<td>Reflectance of GaAs irradiated at 532 nm wavelength</td>
</tr>
<tr>
<td>9-21</td>
<td>Reflectance of CdTe irradiated at 532 nm wavelength</td>
</tr>
<tr>
<td>9-22</td>
<td>Peak reflectance of GaAs and CdTe irradiated at 532 nm wavelength</td>
</tr>
<tr>
<td>A-1</td>
<td>THz and mid-IR spectrum of pentolite powder</td>
</tr>
<tr>
<td>A-2</td>
<td>THz and mid-IR spectrum of HMX powder</td>
</tr>
<tr>
<td>A-3</td>
<td>THz and mid-IR spectrum of RDX powder</td>
</tr>
</tbody>
</table>
PART I

THz spectroscopy and laser-induced infrared emission spectroscopy of nitromethane
Chapter 1
Introduction

For obvious reasons, technologies to detect hazardous materials such as explosives, chemical and biological agents are strongly needed and great amounts of efforts and resources are being spent to explore various forms of detection. Typically, any detection scheme can be classified under either a direct or indirect detection. In the direct detection, hazardous materials are detected and identified simultaneously whereas in the indirect detection, other components of hazardous devises such as triggering mechanisms, dispersion mechanisms and sometimes even likely locations such devices may be hidden are detected. An obvious advantage of direct detection is that it not only detects the presence of the hazardous material but also identifies the material as well. However, the disadvantage is that the detectability could be extremely low because the detection probe (typically some kind of radiation) must actually reach the material and the signal must be returned. This means that the detection probe must penetrate everything which stands between the source, target, and detector. On the other hand, indirect detection provides better detectability since it focuses on the most detectable component. However, disadvantages of the indirect detection are that it is susceptible to false positives and it lacks the ability to identify the hazardous material.

Even in the case of the indirect detection, identifying a hazardous material will eventually be necessary. One way to identify a hazardous material is by studying the responses to the electromagnetic radiation such as absorption (transmittance), reflection, and fluorescence. While spectral features of many hazardous materials have already been
studied\textsuperscript{1-7}, recent advances in the terahertz (THz) technology have fueled a strong interest in research involving THz radiation which was previously unexplored. Some current key research areas include screening, imaging and remote sensing using THz radiation. Recent growth in the interests of THz radiation can be seen in FIG. (1-1) which shows the number of related articles published in the peer reviewed journals.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig1.png}
\caption{The number of THz radiation related articles published in peer reviewed journals.}
\end{figure}

The THz radiation typically refers to electromagnetic (EM) radiation whose frequency falls in the range 0.3 $\sim$ 10 THz (equivalently 10 $\sim$ 333 cm\textsuperscript{-1} wavenumber or 1 mm $\sim$ 33 $\mu$m wavelength.) This frequency range had often been referred to as the "gap" between photonics and electronics. On the high frequency side of the THz radiation,
from UV to mid-infrared, photonics and thermal sources such as lasers and blackbody sources have been effectively used to generate the radiation. On the low frequency side of the THz radiation, from radio wave to microwave, electronics are commonly used. However, it was not until recently that both photonics and electronics became available to provide THz radiation sources, thus, filling the "gap". Some of currently commercially available THz radiation sources include the femtosecond laser driven Auston emitter, molecular laser, and frequency multiplied backward wave oscillator (BWO). One of the best quality THz radiation source is obtained from an accelerator driven system such as the University of Hawaii THz free electron laser (UH THz FEL) which can generate a tunable (0.38 ~ 1.2 THz) high power (~ kW) quasi-continuous wave narrow band ($\Delta \omega / \omega \sim 10^{-8}$) THz radiation beam according to its specification.

One advantage of detecting or imaging hazardous materials using the THz radiation is its ability to penetrate non-metallic materials. Many packaging and clothing materials that are often used to conceal hazardous materials (e.g. paper, plastic, cotton, etc.) are transparent in the THz frequency range. THz transmission spectra of some common packaging materials (cardboard, Styrofoam and sponge foam) which were obtained by our Bruker IFS 66v/S Fourier transform spectrometer (FTIR) (cardboard, Styrofoam and sponge foam) are shown in FIG (1-2). Since many hazardous materials exhibit distinct absorption lines in the THz frequency range, by inspecting a THz spectrum, a hazardous material may be detected and indentified.
Figure 1-2. Transmittance of common packing materials [0.318 cm (1/8 inch) thick cardboard, 2.54 cm (1 inch) thick sponge packing foam (gray), 2.54 cm (1 inch) Styrofoam] in the THz frequency range (12 ~ 100 cm⁻¹).

Compared to the conventional X-ray screening, THz radiation can be more attractive when screening a package or person for hazardous materials. The X-ray screening provides an image based on the density of the materials. Therefore, it is difficult to distinguish materials which have the same shape, size and density but are fundamentally different in chemical compositions. For example, some highly hazardous explosives have similar densities as common household and food items such as toothpaste, hair gel, liquid soap, mustard, cheese, jam, honey, margarine, peanut butter, etc. Hence, it is difficult to distinguish between the tube filled with toothpaste and the tube filled with an explosive by inspecting an X-ray image. Another disadvantage of the
X-ray screening process is that it cannot be used to screen a person due to the obvious health hazard associated with the ionizing radiation. On the other hand, THz imaging can provide spectral signatures as well as a density image of concealed hazardous materials and also poses no significant health risks.

One way to remotely detect and identify a hazardous material is to send an electromagnetic wave (e.g. radio wave, infrared, etc.) and analyze the returned signal. When molecules are irradiated with an infrared laser whose frequency coincides with a vibrational transition frequency of the molecule, the molecules are excited to a higher vibrational state. The excited molecules eventually decay to the thermal equilibrium state by a series of collisions and radiative emissions. So it is possible to identify or remotely sense hazardous materials by analyzing the emitted spectrum followed by the laser irradiation.

Motivated by current strong interests in the THz technology and remote sensing technology needed to detect and identify hazardous materials, THz spectroscopy and CO₂ laser induced IR emission spectroscopy of nitromethane (CH₃NO₂) are presented.

CH₃NO₂ is one of the simplest explosive compounds containing single nitro functional group and it is the prototype of other more powerful explosives such as TNT, HMX and RDX. Also CH₃NO₂ is a readily available hazardous material often used in a high performance racing fuel and can become highly explosive when it is mixed with a fertilizer (ammonium nitrate). The great destructive power of such mixture was witnessed in the tragedy of the 1995 Oklahoma City bombing. CH₃NO₂ was chosen to be studied for its similarity to other explosives and the fact that its THz and laser induced IR emission spectra has not been fully studied.
The earlier spectral study of CH$_3$NO$_2$ dates back to the 1950s. CH$_3$NO$_2$ consists of a free internal rotor, the property by which the methyl rotor (CH$_3$) rotates nearly freely about the NO$_2$ frame. Such motion is an extreme case of a torsional vibrational mode. If a molecule contains an internal rotator (low torsional potential barrier), there is a strong coupling between the rotational and torsional modes and CH$_3$NO$_2$ has often been chosen to study mechanism and effects of this coupling.

One of the first studies conducted on microwave spectra of CH$_3$NO$_2$ is reported by Tannenbaum et al. who obtained the rotational constants and torsional potential barrier height of CH$_3$NO$_2$ and deuterium substituted CD$_3$NO$_2$ from microwave spectra. After Watson developed a reduced Hamiltonian (e.g. Watson's A-reduced Hamiltonian), the rotational constants and the centrifugal distortion coefficients were refined by Rohart who assigned over 130 rotational-torsional transition lines and some of coefficients Rohart reported are still being used in more recent literatures. Later, Sorensen et al. further analyzed the molecular symmetry and suggested that the molecular symmetry allows for the presence of additional terms in the Hamiltonian and showed that the microwave spectrum of CH$_3$NO$_2$ and CD$_3$NO$_2$ are best fitted when these additional terms are included. Furthermore, Sorensen et al. were also able to determine the preferred torsional configuration (orientation of the methyl rotor with respect to the NO$_2$ frame) which corresponds to the lowest point of the potential energy.

In addition to the rotational-torsional spectrum in the microwave region, numerous theoretical and experimental studies of both infrared and Raman spectra of CH$_3$NO$_2$ and its isotopologues are found in numerous papers. As more advanced light sources (e.g. femtosecond laser) became available, recent emphases in the spectral
study have shifted to, but not limited to, the molecular energy transfer dynamics, high resolution overtone spectroscopy and non-linear effect study\textsuperscript{22,23}. While the spectrum of \text{CH}_3\text{NO}_2 in the frequency range from microwave to UV has been studied, its spectrum in the THz frequency range has yet to be fully understood. Spectral features in this range are of importance because this is where the strongest rotational-torsional transitions of \text{CH}_3\text{NO}_2 occur, and it will be discussed in depth in this work.
Chapter 2
Molecular Hamiltonian and absorption coefficients: Review

2.1 Rotational and vibrational Hamiltonian

Simply explained, the THz radiation interacts with molecules in the gas phase by exciting a rotational and vibrational level of a molecule. The pure rotational transitions of many molecules at room temperature are observed in the microwave to THz frequency range and vibrational transitions of some molecules start in the THz frequency range extending to the infrared. Before going into the detail of THz spectrum of CH₃NO₂, it is helpful to briefly review rotational and vibrational states of a molecule, absorption spectra and absorption coefficients.

The rotational-vibrational-electronic (rovibronic) states of a molecule can be obtained by solving the Schrödinger’s equation

\[ \hat{H}\psi = (\hat{\mathcal{T}} + \hat{\mathcal{V}})\psi = E\psi \]  (2-1)

where \( \hat{\mathcal{T}} \) is kinetic energy operator of both nuclei and electrons. \( \hat{\mathcal{V}} \) in this case is a Coulomb potential operator. In this section, it will be shown how Eq. (2-1) can be separated into three Hamiltonians describing the translational, rotational-vibrational and electronic states of the molecule and how the rotational-vibrational Hamiltonian is further separated into the rotational and vibrational Hamiltonians in a zeroth order approximation.

The framework of this section is found in standard spectroscopy text books²⁴,²⁵. The
purpose of including this section is to provide an overview for those who are less familiar to molecular physics or physical chemistry.

Consider a case in which there are \( N \) nuclei and \( n \) electrons and let \((X_i, Y_i, Z_i)\) represent a position of the \( i \)th particle which could be either an electron or a nucleus in the lab frame. Then the kinetic energy operator \( \hat{T} \) is then given by

\[
\hat{T} = -\sum_{i=1}^{n+N} \frac{\hbar^2}{2m_i} \left( \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right)
\]

which depends on \( 3(n+N) \) variables. By introducing a new coordinate \((x, y, z)\) which is parallel to the lab frame and whose origin is located at the center of mass \((X_C, Y_C, Z_C)\), positions of particles are expressed as

\[
X_i = X_C + x_i
\]
\[
X_C = \frac{1}{M} \sum_{i=1}^{N} m_i X_i
\]

where \( M \) is the total mass of a molecule and \( m \) is a nuclear mass. Strictly speaking, the summation in EQ. (2-4) should include all the electrons; however, because of large mass differences between the electrons and the nuclei, only the nuclei are counted in EQ. (2-4). From EQ. (2-3) and EQ. (2-4), the position of one of the nuclei can be written in terms of the positions of the rest of nuclei. For example, \( x_1 \) can be written as

\[
x_1 = -\frac{1}{m_1} \sum_{i=2}^{N} m_i x_i
\]

By directly substituting EQ. (2-3) into EQ. (2-2) and substituting EQ. (2-5) for \( x_1, y_1, \) and \( z_1 \), it can be shown that the \( \hat{T} \) becomes
The first term represents the translational energy of a molecule and the second term represents the internal rotational-vibrational-electronic (rovibronic) kinetic energy which now depends on \(3(n + N) - 3\) independent variables.

The Coulomb potential energy \(\hat{V}\) in EQ. (2-1) is given by

\[
\hat{V} = \frac{1}{4\pi\varepsilon_0} \sum_{i=1}^{n+N} \sum_{j=1}^{N} \frac{Q_i Q_j}{\sqrt{(x_i-x_j)^2 + (y_i-y_j)^2 + (z_i-z_j)^2}}
\]

where \(Q_i\) are electric charges of nuclei and electrons. Since this potential only depends on interparticle distances and not on the center of mass coordinates, translational kinetic energy term of the Hamiltonian can be separated from the full Hamiltonian

\[
\hat{T} = -\frac{\hbar^2}{2M} \left( \frac{\partial^2}{\partial X_C^2} + \frac{\partial^2}{\partial Y_C^2} + \frac{\partial^2}{\partial Z_C^2} \right) + \hat{T}_{\text{rovib}}
\]

\[
(\hat{T}_{\text{rovib}} + \hat{V}) \psi_{\text{rovib}} = E_{\text{rovib}} \psi_{\text{rovib}}
\]

\[
E = E_T + E_{\text{rovib}}
\]

where \(E_{\text{rovib}}\) and \(\psi_{\text{rovib}}\) are rovibronic energy and wavefunction. The translational energy \(E_T\) is continuous and does not affect spectral characteristics of the molecule, thus it will not be discussed any further.

The rotational-vibrational-electronic Hamiltonian in EQ. (2-9) can be further separated into two equations, rotational-vibrational and electronic parts. Let \(R\) and \(r\) be the positions of nuclei and electrons from the center of the mass, then, EQ. (2-9) becomes
The first and second terms on the left side are kinetic energies of the nuclei and the electrons. \( \hat{V}_n^e \) and \( \hat{V}_c^e \) are the coulomb repulsion potentials of nuclei and electrons and \( \hat{V}_n^e \) is the coulomb attraction potential between nuclei and electrons. Generally, EQ. (2-11) is difficult to solve without the Born-Oppenheimer approximation\(^{26} \). The Born-Oppenheimer approximation approximates that the electrons "see" the nuclei as fixed particles. While electrons feel the potential from the nuclei, the motions of the nuclei (small oscillation around the equilibrium position) do not affect the motion of the electrons. If the wavefunction is assume to take the form \( \psi_{re} = \psi_e(R, r) \psi_{re}(R) \) and substituted into EQ. (2-11), then in the Born-Oppenheimer approximation, the terms containing \( \nabla_R \psi_e(R, r) \) and \( \nabla_R \psi_e(R, r) \) are neglected\(^{25} \). Then, EQ. (2-11) becomes

\[
\left( -\frac{\hbar^2}{2m_e} \sum_{j=1}^{n} \frac{1}{m_j} \nabla_{\vec{r}_j}^2 + \hat{V}_n^e (R, r) + \hat{V}_c^e (r) \right) \psi_e(R, r) = \hat{V}_{elec}^i (R) \psi_e(R, r)
\]

EQ. (2-12)

\[
\left( -\frac{\hbar^2}{2} \sum_{j=1}^{n} \frac{1}{m_j} \nabla_{\vec{r}_j}^2 + \hat{V}_n^e (R) - \hat{V}_{elec}^i (R) \right) \psi_{re}^i (R) = E \psi_{re}^i (R)
\]

EQ. (2-13)

In solving EQ. (2-12), the nucleus coordinates \( R \) are treated as parameters which define the potential energy that electrons feel while 3\( n \) electron coordinates are treated as independent variables. The energy levels \( \hat{V}_{elec}^i (R) \) obtained from EQ. (2-12) depend on the nuclear coordinates \( R \) and must appear as an additional potential energy in EQ. (2-13). Since each \( \hat{V}_{elec}^i (R) \) is a different function of \( R \), the rotational-vibrational wavefunction \( \psi_{re}^i \) and the rotational-vibrational energy levels \( E_{re}^i \) must be calculated for a
specific $\tilde{V}_e^i (R)$. In general, the electronic energy level $E_e^i$ is defined at the lowest point of the potential energy $\tilde{V}_e (R) - \tilde{V}_e^i (R)$ and the rotational-vibrational energy is measured from the electronic energy level

$$E_{\text{rv}}^i = E - E_e^i$$  \hspace{1cm} (2-14)

The schematic description of electronic and rovibrational energy levels are shown in FIG. (2-1).

![Schematic description of electronic and rovibrational energy levels of a molecule. $E_{\text{rv}}^i$ represents $j^{th}$ rotational-vibrational level of the $i^{th}$ electronic level.](image)

**Figure 2-1.** Schematic description of electronic and rovibrational energy levels of a molecule. $E_{\text{rv}}^i$ represents $j^{th}$ rotational-vibrational level of the $i^{th}$ electronic level.

Typically the energy required to electronically excite a molecule ranges from a few eV to tens of eV. Since transitions between electronic states are not involved in the
THz spectroscopy or the CO$_2$ laser-induced IR emission spectroscopy, all molecules are considered to be in the electronic ground state. Thus, the electronic state of the molecule will not be discussed further.

Having separated translational and electronic Hamiltonians from the original Hamiltonian, the next step is to split EQ. (2-13) into rotational and vibrational Hamiltonians. The classical form of the Hamiltonian in EQ. (2-13) is given by

$$H_r = \frac{1}{2} \sum_{i=1}^{N} m_i \dot{R}_i^2 + V(R) \tag{2-15}$$

where $R_i$ are coordinates in the space-fixed axis system which is parallel to the lab axes whose origin is at the center of mass. Now consider a molecule-fixed axis system which is allowed to rotate in the space with the molecule. Then, the velocity vector $\dot{R}$ in the rotating molecule-fixed coordinate is given by

$$\dot{R} = \omega \times \rho + \dot{\rho} \tag{2-16}$$

where $\omega$ is an angular velocity of the rotating axes and $\rho$ is a position of a nucleus in the molecule-fixed axis system. Substituting EQ. (2-16) into EQ. (2-15), the classical Hamiltonian becomes

$$H_{rv} = \frac{1}{2} \sum_{i=1}^{N} m_i |\omega \times \rho_i|^2 + \frac{1}{2} \sum_{i=1}^{N} m_i \dot{\rho}_i^2 + V(\rho) + \omega \cdot \sum_{i=1}^{N} m_i \rho_i \times \dot{\rho}_i \tag{2-17}$$

EQ. (2-17) can not be separated into rotational and vibrational Hamiltonians because of the coupling term $H_{rv}$. However, noting that atoms in a molecule undergo small oscillations about an equilibrium position, $H_{rv}$ can be minimized if the molecule-fixed coordinate is defined by the condition
\[ \sum_{i=1}^{N} m_i \xi_i \times \rho_i = 0 \]  
\[ \text{(2-18)} \]

which directly leads to

\[ \sum_{i=1}^{N} m_i \xi_i \times \dot{\rho}_i = 0 \]  
\[ \text{(2-19)} \]

where \( \xi \) is the equilibrium position. EQ. (2-18) is called the Eckart condition\(^ {27} \). Let

\[ \eta = \rho - \xi \]. Then, from EQ. (2-19), \( H_{\nu} \) becomes

\[ H_{\nu}' = \omega \cdot \sum_{i=1}^{N} m_i \eta_i \times \dot{\rho}_i \]  
\[ \text{(2-20)} \]

which is indeed small if the amplitude of the oscillation is small \( (\rho = \xi) \). Similarly

using EQ. (2-18), \( H_r \) in EQ. (2-17) becomes

\[ H_r = \frac{1}{2} \sum_{i=1}^{N} m_i |\omega \times \xi_i|^2 - \sum_{i=1}^{N} m_i (\omega \times \xi_i) \cdot (\omega \times \eta_i) + \frac{1}{2} \sum_{i=1}^{N} m_i |\omega \times \eta_i|^2 \]  
\[ \text{(2-21)} \]

\( H_r^\theta \) represents the energy of a rigid-rotor. Defining the set of axes which diagonalize the moment of inertia tensor to be \( a, b \) and \( c \), \( H_r^\theta \) is expressed as

\[ H_r^\theta = \frac{1}{2} \left( \frac{I_a}{I_a}^2 + \frac{L_a^2}{I_a} + \frac{L_c^2}{I_c} \right) \]  
\[ \text{(2-22)} \]

where \( L_i \) \( (L_i = I_i \omega) \) and \( I_i \) are components of the angular momentum and the moment of inertia along the axis \( a, b, \) or \( c \). In the rigid-rotor approximation \( (\text{i.e. } \rho = \xi) \), the Eckart condition is satisfied by choosing the molecule-fixed axes to coincide with \( a, b, \) or \( c \).

Recalling that \( \eta \) represents the displacement from the equilibrium position,

\[ V(\rho) \text{ in EQ. (2-17) can be expanded in terms of } \eta_i = \eta_{11} \hat{x} + \eta_{12} \hat{y} + \eta_{13} \hat{z} \]
where the constant term in the expansion is set to zero and the first derivative term is also zero because the net force is zero when all atoms are at the equilibrium positions. After separating the translational and electronic Hamiltonians from the original Hamiltonian, there are total of \(3N - 3\) independent variables in \(H_v\). Since there are three independent variables in the rotational Hamiltonian \(H_r^0\) (with exception of a linear molecule which only has two axes of rotation), there must only be \(3N - 6\) independent variables for the vibrational Hamiltonian \(H_v^0\). This means that diagonalizing a \(3N \times 3N\) vibrational Hamiltonian matrix whose components are given by

\[
H_v^0 = \frac{1}{2} \sum_{i=1}^{N} m_i \dot{\eta}_i^2 + \frac{1}{2} \left[ \sum_{i=1}^{N} (\eta_i \cdot \nabla_i) \right]^2 V + \cdots
\]

(2-23)

\[
\frac{\partial^2 V}{\partial \eta_i^2} |_{\eta_i = \eta_i^0} \frac{\eta_i^2}{2}
\]

(2-24)

\[
\frac{\partial^2 V}{\partial \eta_i \partial \eta_j} |_{\eta_i = \eta_i^0} \eta_i \eta_j
\]

yields \(3N - 6\) eigenvectors which are called normal vibrational coordinates. In terms of normal coordinate \(q_i\), \(H_v^0\) can be written as

\[
H_v^0 = \sum_{i=1}^{3N-6} \left( \frac{1}{2} \mu_i \dot{q}_i^2 + \frac{1}{2} k_i q_i^2 \right)
\]

(2-25)

where \(\mu\) and \(k\) are constants obtained upon diagonalizing Eq. (2-24).

The zeroth order rotational-vibrational energy levels are obtained by solving two separate Schrödinger’s equations for \(\hat{H}_r^0\) and \(\hat{H}_v^0\) whose quantum mechanical expressions are given by
\[
\hat{H}_r^0 = \frac{1}{2} \left( \frac{\hat{j}_a^2}{I_a} + \frac{\hat{j}_b^2}{I_b} + \frac{\hat{j}_c^2}{I_c} \right) 
\]
(2-26)

\[
\hat{H}_r^0 = \sum_{ij} \left( -\frac{\hbar^2}{2\mu_i} \nabla_{\phi_i}^2 + \frac{1}{2} k_i \phi_i^2 \right) 
\]
(2-27)

where \( \hat{j}_a, \hat{j}_b \) and \( \hat{j}_c \) are the angular momentum operators along molecule-fixed axes. By introducing the ladder operators \( \hat{j}_\pm = \hat{j}_b \pm i\hat{j}_c \) and the total angular momentum operator \( \hat{j}^2 = \hat{j}_a^2 + \hat{j}_b^2 + \hat{j}_c^2 \), Eq. (2-26) can be written as\(^{24}\)

\[
\hat{H}_r^0 = \frac{1}{2} (B+C) \hat{j}^2 + \left( A - \frac{1}{2} (B+C) \right) \hat{j}_a^2 + \frac{1}{4} (B-C)(\hat{j}_b^2 + \hat{j}_c^2) 
\]
(2-28)

When solving the Schrödinger's equation \( \hat{H}_r^0 \phi_r = E_r^0 \phi_r \), the wavefunction \( \phi_r \) can be expanded in the orthogonal basis set \( |J, k, M\rangle \) where \( J \) is a quantum number for \( \hat{j}^2 \) which takes a positive integer, \( k \) and \( M \) are quantum numbers of \( \hat{j}_a \) and \( \hat{j}_c \) which take an integer ranging from \(-J\) to \(J\). \( \hat{j}_a \) is the angular momentum operator along the space-fixed \( z \) axis which is absent from the Hamiltonian. If the molecule is a symmetric rotor [i.e. \( A > B = C \) (prolate) or \( A = B > C \) (oblate)], the Hamiltonian matrix is diagonal in the \( |J, k, M\rangle \) representation. Then, it can be shown that the rotational energy level of a symmetric rotor is\(^{24}\)

\[
E_r^0 (J, k) = \hbar^2 \left\{ BJ(J+1) + (A-B)k^2 \right\} \quad \text{if } A > B = C \\
E_r^0 (J, k) = \hbar^2 \left\{ BJ(J+1) + (C-B)k^2 \right\} \quad \text{if } A = B > C 
\]
(2-29)
which is doubly degenerate in \( k \) for \( k \neq 0 \) and \( 2J + 1 \) degenerate in \( M \). If the molecule is asymmetric, the Hamiltonian matrix cannot be diagonalized in the \( |J, k, M\rangle \) basis due to the ladder operators in EQ. (2-28). Thus, \( k \) will no longer be a good quantum number.

By convention, the rotational state of an asymmetric rotor is often labeled as \( J K_a K_c \), where \( K_a \) and \( K_c \) represent values of \( k \) in the limit of prolate and oblate symmetric rotors. For example, an asymmetric rotational energy of \( (2 2 1) \) in the \( (J K_a K_c) \) representation is approximately same to the symmetric rotational energy of \( (2 2) \) if the rotor is near prolate and \( (2 1) \) if the rotor is near oblate in the \( (J k) \) representation.

From EQ. (2-27), it is seen that the vibrational Hamiltonian \( H_v^0 \) consists of \( 3N - 6 \) independent harmonic oscillators. Therefore, the vibrational state can be represented by \( 3N - 6 \) independent vibrational modes \( |v_1, v_2, v_3, \ldots, v_{3N+6}\rangle \) where each \( v \) can take zero or positive integer and the vibrational energy is given by the sum of each harmonic oscillator energy.

\[
E_v^0 = \hbar \left[ \omega_1 \left( \frac{1}{2} + v_1 \right) + \omega_2 \left( \frac{1}{2} + v_2 \right) + \ldots + \omega_{3N+6} \left( \frac{1}{2} + v_{3N+6} \right) \right] \tag{2-30}
\]

The THz spectrum of CH$_3$NO$_2$ is attributed to transitions involving rotational states and the lowest vibrational mode (torsional mode) and in Chapter 3, the method of calculating transition frequencies and intensities between rotational-torsional states will be described. In the calculation, the rotational Hamiltonian shown in EQ. (2-21) will be expanded in terms of the angular momentum operator \( \hat{J} \) and \( \hat{J}_z \). The expanded Hamiltonian is called Watson's A-reduced Hamiltonian. In Chapter 3, the rotational-torsional Hamiltonian of CH$_3$NO$_2$ will be developed and it will be shown that the
rotational-torsional Hamiltonian will include the Watson's A-reduced Hamiltonian, the
tortional Hamiltonian and the coupling term.

2.2 Radiation interaction

When electromagnetic radiation is incident on a molecule, the molecule can be excited to a higher state by absorbing a photon. The probability for a transition to occur is greatest when the photon energy corresponds to the transition energy and it is well known that the transition probability between two states via absorption or emission of a photon is proportional to an absolute value squared electric dipole moment matrix element

\[ P_{n \rightarrow m} \propto |\langle n | \hat{\mu} | m \rangle|^2 \]  
(2-31)

where \( m \) and \( n \) are the initial and the final state and \( \hat{\mu} \) is an electric dipole moment operator in the space-fixed axes. The transitions are allowed only if the electric dipole moment matrix elements are non-vanishing.

An electric dipole moment \( \hat{\mu} \) in the space-fixed axes can be written in terms of the dipole moment in the molecule-fixed axes. For example, the \( x \) component of \( \hat{\mu} \) is given by\textsuperscript{25}

\[ \hat{\mu}_x = \sum_{g=a,b,c} \phi_{gx} \hat{\mu}_g \]  
(2-32)

where \( \phi \) is called the "direction cosine" operator which depends on the three Euler angles that define the orientation between the space-fixed and the molecule-fixed axes.
\( \mu_x, \mu_y \) and \( \mu_z \) are components of a dipole moment along the molecule-fixed axes. If \( \mu \) in EQ. (2-32) is expanded in terms of the \( 3N - 6 \) vibrational coordinates, EQ. (2-32) becomes

\[
\mu_x = \sum_{g=a,b,c} \phi_{gx} \left( \mu_{g0} + \sum_{i=1}^{3N-6} \frac{\partial \mu}{\partial q_i} \hat{q}_i \right) + \frac{1}{2} \sum_{j=1}^{3N-6} \sum_{i=1}^{3N-6} \frac{\partial^2 \mu}{\partial q_i \partial q_j} \hat{q}_i \hat{q}_j + \cdots \quad (2-33)
\]

By writing a rotational-vibrational state of a molecule as a combination of rotational state \(| J, K_a, K_c \rangle \) described in the previous section (Sec. 2.2) and the quantum numbers for \( 3N - 6 \) vibrational modes \(| v_1, v_2, \ldots, v_{3N-6} \rangle \), the rotational-vibrational state of a molecule can be expressed as \( \psi_r = | J, K_a, K_c \rangle \otimes | v_1, v_2, \ldots, v_{3N-6} \rangle \). Then, in this notation, the transition probability is proportional to

\[
P \propto \left| \left\{ v_1, v_2, \ldots, v_{3N-6} \right\} \otimes \left\{ J', K_a', K_c' \right\} \hat{\mu} \left[ | J, K_a, K_c \rangle \otimes | v_1, v_2, \ldots, v_{3N-6} \rangle \right] \right|^2 = \sum_{w=x,y,z} \sum_{g=a,b,c} \sum_{h=1}^{3N-6} \langle J', K_a', K_c' | \phi_{gw} | J, K_a, K_c \rangle \left( \mu_{g0} \right.
\]

\[
+ \sum_{i=1}^{3N-6} \alpha_{gi} \langle v_1, v_2, \ldots, v_{3N-6} | \hat{q}_i | v_1, v_2, \ldots, v_{3N-6} \rangle
\]

\[
+ \sum_{i=1}^{3N-6} \sum_{j=1}^{3N-6} \beta_{gij} \langle v_1, v_2, \ldots, v_{3N-6} | \hat{q}_i \hat{q}_j | v_1, v_2, \ldots, v_{3N-6} \rangle + \cdots \right) \right|^2 \quad (2-34)
\]

where

\[
\alpha_{gi} = \left. \frac{\partial \mu}{\partial q_i} \right|_0 \quad \beta_{gij} = \frac{1}{2} \left. \frac{\partial^2 \mu}{\partial q_i \partial q_j} \right|_0
\]

The first term represents pure rotational transitions which are non-zero only if a molecule has a permanent dipole moment (i.e. \( \mu_{g0} \neq 0 \)). The second term represents vibrational transitions which are linear in \( \hat{q}_i \). From the usual quantum mechanical
treatment of a harmonic oscillator, \( \hat{q}_i \) can either raise or lower the quantum number \( \nu_j \) by one. In addition, \( \alpha_{gi} \) must be non-zero in order for the transition to be allowed. The vibrational transitions with non-zero \( \alpha_{gi} \) are called IR active and the transitions whose \( \alpha_{gi} \) is zero are called IR inactive. The last term in \( \text{EQ. (2-34)} \) represents the second order vibrational transitions. This term can raise or lower the levels of two vibrational modes by one (combination) or single vibrational mode by two (overtone).

It is seen from \( \text{EQ. (2-34)} \) that any vibrational transitions must accompany a simultaneous rotational transition. Depending on the concurring rotational transition, there are three types of branches in a vibrational band. Let \( \Delta J = J_f - J_i \) and \( J_i, J_f \) be the initial and final rotational quantum number \( J \) respectively. The vibrational transitions which are accompanied by \( \Delta J = -1, 0, 1 \) rotational transitions are called P-branch, Q-branch and R-branch respectively. FIG. (2-2) is a spectrum of CO\(_2\) acquired with our IFS 66 v/S FTIR which shows the vibrational transition centered at 672 cm\(^{-1}\) and all three accompanying branches.
Figure 2-2. Absorption spectrum of CO$_2$ showing the vibrational transition at 672 cm$^{-1}$. Three branches of concurring rotational transitions are shown.
2.3 Absorption coefficient

An absorption coefficient $\alpha(\tilde{\nu})$ of a molecule is related to a measured transmittance $T$ by

$$T = \exp[-\ell n\alpha(\tilde{\nu})]$$

(2-35)

where $\ell$ is a propagation length, $n$ is molecular density and $\tilde{\nu}$ is the wavenumber. The absorption coefficient $\alpha(\tilde{\nu})$ is obtained by summing all transitions intensities which are multiplied by their line shape functions $W$

$$\alpha(\tilde{\nu}) = \sum A_{i\rightarrow f} W_{i\rightarrow f}(\tilde{\nu} - \tilde{\nu}_{fi})$$

(2-36)

where $i \rightarrow f$ indicates the transition from the initial state $i$ to the final state $f$ and $\tilde{\nu}_{fi}$ is the transition wavenumber $\tilde{\nu}_{fi} = \tilde{\nu}_f - \tilde{\nu}_i$. A line shape function $W$ accounts for the broadening effects such as natural broadening, pressure broadening and the Doppler broadenings and normalized to unity. $W$ typically takes the form of either a Lorentzian, a Gaussian or a Voigt (Lorentzian convoluted with Gaussian) function depending on the dominant broadening effect. $A_{i\rightarrow f}$ is a line integrated absorption coefficient given by

$$A_{i\rightarrow f} = \frac{8\pi^3}{3hc} \tilde{\nu}_{fi} (F_i - F_f) D_{i\rightarrow f}$$

(2-37)

where $F_i$ and $F_f$ are fractions of molecules in the initial and the final state which are given by the usual Boltzmann distribution.

$$F_i = \frac{\exp\left(-\frac{\tilde{\nu}_i}{k_BT}\right)}{G}$$

(2-38)
where \( \tilde{k}_B = k_B/hc = 0.695039 \text{ cm}^{-1}/K \), \( T \) is a temperature and \( G \) is a partition function and \( D_{i \rightarrow f} \) is an electric dipole transition matrix element summed over all degenerate states.

One advantage of THz spectroscopy is that rotational transitions are often strongest in the THz frequency range. In the zeroth order approximation, the rotational energy (in units of wavenumbers) is given by

\[
\tilde{\nu} = \tilde{B} J (J+1)
\]  

(2-39)

and the transition energy from \( J_i \) to \( J_{i+1} \) is given by

\[
\tilde{\nu}_{fi} \sim 2 \tilde{B} (J_i + 1)
\]  

(2-40)

Since each rotational level is at least \( 2J + 1 \) degenerate, the degeneracy is proportional to \( \tilde{\nu}_{fi} \). Thus, from EQ. (2-37) and EQ. (2-38), the intensity of a pure rotational transition is proportional to

\[
A_{i \rightarrow f} \propto \tilde{\nu}_{fi} \exp \left( \frac{-\tilde{\nu}_{fi}}{k_BT} \right) \left[ 1 - \exp \left( \frac{-\tilde{\nu}_{fi}}{k_BT} \right) \right] \tilde{\nu}_{fi}
\]  

(2-41)

and in the limit of \( \tilde{\nu}_i - \tilde{\nu}_{fi} \ll \tilde{k}_B T \), it can be shown that \( A_{i \rightarrow f} \) increases roughly as \( \tilde{\nu}_{fi}^3 \).

Thus, in this case, the absorption coefficients in the THz frequency range are greater than those in the microwave range. FIG. (2-3) shows calculated pure rotational spectra of symmetric molecules in various sizes at 300 K which clearly shows that the strongest rotational transitions occurring in the THz frequency range. The calculation was carried out by using EQ. (2-27) and EQ. (2.37). The squared electric dipole transition moment \( D \) appearing in EQ. (2.37) was calculated in the same way it is described in Chapter 3.
Figure 2-3. Calculated line integrated absorption coefficients of oblate rotors in various sizes ($A/C = 10$).
Chapter 3
Rotational-torsional levels and absorption coefficients of CH$_3$NO$_2$

3.1 Rotational-torsional levels

Figure 3-1. Geometrical configuration of CH$_3$NO$_2$ (not actual scale)

FIG. (3-1) shows the geometrical configuration of CH$_3$NO$_2$. CH$_3$NO$_2$ consists of a heavy frame (NO$_2$) and a light internal methyl (CH$_3$) rotator. In this section, the molecule-fixed axes are labeled as (a, b, c) which are depicted in FIG. (3-1). The molecule-fixed axes diagonalize the moment of inertial matrix. In addition to the molecule-fixed axes, (x, y, z) will be used to label the space-fixed axes which are parallel to the “lab frame” axes and the origin is located at the center of mass. Because of the low torsional potential barrier height$^{14}$ (~2 cm$^{-1}$), the methyl rotator is virtually free to rotate. The lowest vibrational mode, excluding the torsional mode, of CH$_3$NO$_2$ is 470 cm$^{-1}$.

According to the Boltzmann distribution, the ratio of molecules in the first vibrationally
excited state to the ground state is 0.1 at room temperature (300 K). Consequently, only the molecule in the ground state will be considered here.

In the calculations that follow, the energy (or frequency) will be expressed in the unit of wavenumber (cm\(^{-1}\)) \(\tilde{\nu}\) which is directly related to the actual energy \(E\) by \(\tilde{\nu} = \frac{E}{hc}\) where \(h\) is the Planck's constant and \(c\) is the speed of light. In the previous section, the rotational-vibrational Hamiltonian was separated into rotational and vibrational parts with the assumption that the atoms undergo small oscillations about their equilibrium positions. However, when a molecule consists of an internal rotator as CH\(_3\)NO\(_2\) does, that assumption is no longer correct since the methyl rotator is free to rotate instead of wiggling around the equilibrium position. Instead of treating the rotational and torsional Hamiltonians separately, the rotational-torsional Hamiltonian which includes coupling term and torsional potential barrier must be used to calculate the rotational-torsional levels. The rotational-torsional Hamiltonian is given by\(^{14}\)

\[
\hat{H} = \hat{H}_{\text{rot}} + F j_m^2 - 2 A' \tilde{\nu} + \frac{V_6}{2} (1 - \cos 6\alpha)
\]

where \(\hat{H}_{\text{rot}}\) is the type I' (\(A > B > C\)) Watson's A-reduced rotational Hamiltonian\(^{10-12}\)

\[
\hat{H}_{\text{rot}} = \frac{1}{2} (B+C) \tilde{j}_2 + \left( A - \frac{1}{2} (B+C) \right) \tilde{j}_4 - A_j \tilde{j}_4 - (F \tilde{j}_2) - A' \tilde{j}_4 + \frac{1}{4} (B-C) (\tilde{j}_2^2 + \tilde{j}_4^2) - \delta_j \tilde{j}_2 \left( \tilde{j}_4^2 + \tilde{j}_2^2 \right) - \frac{\delta_2}{2} \left[ \tilde{j}_a^2 \left( \tilde{j}_2^2 + \tilde{j}_4^2 \right) + \left( \tilde{j}_2 \tilde{j}_4 \right) \tilde{j}_a^2 \right]
\]

where \(A, B, C\) are rotational constants of the CH\(_3\)NO\(_2\). \(F\) is a torsional constant of the methyl rotor about the C-N axis ("a" axis in FIG. 1), \(A'\) is a rotational-torsional coupling constant, \(V_6\) is the height of the torsional barrier potential (2.1 cm\(^{-1}\)), and \(A_j, A_\mu, A, \delta_j, \delta_2\),

27
and \( \delta_k \) are centrifugal distortion constants. \( \hat{j}_m \) in EQ. (3-1) is an angular momentum operator of the methyl rotor along the C-N axis and given by

\[
\hat{j}_m = -i\hbar \frac{\partial}{\partial \alpha}
\]

and its eigenfunction is

\[
\phi(\alpha) = \exp(i m \alpha)
\]

The \( \cos(6\alpha) \) term in EQ. (3-1) represents six-fold symmetry of the torsional angle (\( i.e. \) orientations of three hydrogen atoms) which consists of three 60 degrees rotations and their reflection about plane containing NO\(_2\). All constants in EQ. (3-1) and EQ. (3-2) are provided in Table (3-1). These constants were previously determined by fitting the rotational spectrum of CH\(_3\)NO\(_2\) in the microwave region\(^{14}\).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value ((cm^{-1}/h^2))</th>
<th>Parameter</th>
<th>Value ((cm^{-1}/h^4)) except (V_6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A)</td>
<td>0.4450</td>
<td>(\Delta_j)</td>
<td>0.2408\times10^{-6}</td>
</tr>
<tr>
<td>(B)</td>
<td>0.3517</td>
<td>(\Delta_k)</td>
<td>0.5921\times10^{-6}</td>
</tr>
<tr>
<td>(C)</td>
<td>0.1960</td>
<td>(\Delta_k)</td>
<td>-0.2515\times10^{-6}</td>
</tr>
<tr>
<td>(A')</td>
<td>0.4431</td>
<td>(\delta_j)</td>
<td>0.8229\times10^{-7}</td>
</tr>
<tr>
<td>(F)</td>
<td>5.561</td>
<td>(\delta_k)</td>
<td>0.5254\times10^{-6}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(V_6)</td>
<td>2.1 (cm^4)</td>
</tr>
</tbody>
</table>

\(a.\) Ref. (14)

Eigenstates of the Hamiltonian given in EQ. (3-1) can be expanded in the orthogonal basis set \(|m, J, k, M\rangle\) where \(m, J, k, \) and \(M\) are associated with angular momentum operators \(\hat{j}_m, \hat{j}_z, \hat{j}_a, \) and \(\hat{j}_x\) respectively and possible values are
\( m = \ldots -2, -1, 0, 1, 2, \ldots \)
\( J = 0, 1, 2, \ldots \)
\( k = -J, -J+1, \ldots J-1, J \)
\( M = -J, -J+1, \ldots J-1, J \)
\( m + k = \text{even} \) \hfill (3-5)

Note that \( \hat{J}_z \) is an angular momentum operator along the space-fixed z axis which is absent from the Hamiltonian when there is no external field. The "\( m + k = \text{even} \)" restriction arises from the nuclear spin symmetry of \( \text{CH}_3\text{NO}_2 \)\(^{14,24} \). Since the Hamiltonian in EQ. (3-1) is independent of \( M \), each energy level is \( 2J+1 \) degenerate for different values of \( M \). Rotational-torsional energy levels are obtained by diagonalizing the Hamiltonian matrix \( \langle m', J', k', M' | \hat{H} | m, J, k, M \rangle \) which is block-diagonal in \( J \) and \( M \). The diagonal and off-diagonal Hamiltonian matrix elements (suppressing \( h \)) are given by

\[
\langle m, J, k, M | \hat{H} | m, J, k, M \rangle = \left[ \frac{1}{2} (B+C) - \Delta_j J (J+1) - \Delta_k k^2 \right] J (J+1) \\
+ \left[ A - \frac{1}{2} (B+C) - \Delta_k k^2 \right] k^2 + F m^2 - 2 A' k m + \frac{V_6}{2}
\] \hfill (3-6)

\[
\langle m, J, k, M | \hat{H} | m, J, k+2, M \rangle = \left\{ \frac{1}{4} (B-C) - \delta_j J (J+1) - \delta_k [(k+2)^2 + k^2] \right\} \\
\left\{ [J (J+1) - (k+1) k] [J (J+1) - (k+2)(k+1)] \right\}^{1/2}
\] \hfill (3-7)

\[
\langle m, J, k, M | \hat{H} | m+6, J, k, M \rangle = -\frac{V_6}{4}
\] \hfill (3-8)

Since the Hamiltonian has off-diagonal terms in \( k \) and \( m \), only \( J \) remains as a good quantum number. However, at low \( J \) value, a single \( m \) value dominates for each eigenstate except for \( m = -3, 3 \). Thus, \( m \) can also be used as a good quantum number.
According to EQ. (3-5), \( m \) could be any integer. Therefore, when numerically calculating rotational-torsional levels from the above Hamiltonian, \( m \) must be truncated somewhere. The place of truncation was determined by calculating the energy levels by diagonalizing the Hamiltonian matrix given in EQ. (3-6) ~ EQ. (3-9) and evaluating the convergence of calculated energies as the place of truncation is extended. When the number of \( m \) included in the Hamiltonian matrix is increased from \( m = -12, -6, 0, 6, 12 \) to \( m = -18, -12, -6, 0, 6, 12, 18 \), our calculation showed fractional shifts in energy levels to be than \( 1.0 \times 10^{-6} \) for \( J \) up to 120.

The accuracy of calculation was verified by comparing the calculated result to over 130 known rotational transition lines in the microwave region\(^{13} \). While the difference between the calculation and the reported values tends to slightly increase as \( J \) increases, the fractional differences were better than 1\% in all lines which were compared.

### 3.2 Electric dipole transition moments and absorption coefficient

In order to calculate the absorption coefficients after obtaining rotational-torsional energies and eigenstates, degeneracy summed squared dipole transition matrix elements [\( D_{i \rightarrow f} \) in EQ. (2-37)] must be evaluated. The degeneracy arises from nuclear spins, electronic spins and angular momentum \( M \) which are absent from the rotational-torsional Hamiltonian. Taking these degeneracies into account, \( D_{i \rightarrow f} \) is given by\(^{24} \) (non-polarized incident light)
\[ D_{i \rightarrow f} = g_a (2S + 1) \sum_{M_f} \sum_{M_i} \sum_{n=1}^{1} | \langle \psi_f | \hat{\mu}_n | \psi_i \rangle |^2 \]  

(3-9)

where \( g_a \) and \( S \) are nuclear spin and electronic spin quantum numbers, \( x, y, \) and \( z \) are space-fixed coordinates, \( \psi_i \) and \( \psi_f \) are the initial and the final eigenstates. According to REF. (24), the electric dipole moment matrix elements in a space-fixed coordinates can be written in terms of the dipole moment in a molecule-fixed coordinates by introducing \( \hat{\mu}_{z,n} \) and \( \hat{\mu}_{m,l} \) which are defined as

\[
\begin{align*}
\hat{\mu}_{z,0} &= \hat{\mu}_z \\
\hat{\mu}_{z,\pm 1} &= \frac{1}{\sqrt{2}} ( \mp \hat{\mu}_z + i \hat{\mu}_y ) \\
\hat{\mu}_{m,0} &= \hat{\mu}_a \\
\hat{\mu}_{m,\pm 1} &= \frac{1}{\sqrt{2}} ( \mp \hat{\mu}_a + i \hat{\mu}_c )
\end{align*}
\]

(3-10)

where \( a, b \) and \( c \) are the molecule-fixed axes. With this notation, Eq. (3-9) can be rewritten as

\[ D_{i \rightarrow f} = g_a (2S + 1) \sum_{M_f} \sum_{M_i} \sum_{n=1}^{1} | \langle \psi_f | \hat{\mu}_{z,n} | \psi_i \rangle |^2 \]  

(3-11)

and the electric dipole moment matrix elements in \([m, J, k, M]\) basis are given by

\[
\begin{align*}
\langle m, J, k, M | \hat{\mu}_{z,n} | m', J', k', M' \rangle &= \sum_{\ell=1}^{1} \langle m | \hat{\mu}_{m,\ell} | m' \rangle (-1)^{\ell+M} \sqrt{(2J+1)(2J'+1)} \\
&\times \begin{pmatrix} J' & 1 & J \\ k' & \ell & -k \\
M' & n & -M \end{pmatrix} \begin{pmatrix} J_1 & J_2 & J \\ M_1 & M_2 & M \end{pmatrix}
\end{align*}
\]

(3-12)

where \( \begin{pmatrix} J_1 & J_2 & J \\ M_1 & M_2 & M \end{pmatrix} \) is Wigner's 3-j symbol which is related to the Clebsch-Gordan coefficient by
and it can be also shown that

\[ \sum_{J'=J-1}^{J+1} \sum_{M=-J}^{J} (-1)^M \left( \begin{array}{cc} J' & 1 \\ M & -M \end{array} \right)^2 = (2J+1)(2J'+1) \]  

(3-14)

Expressing a rotational-torsional eigenstate corresponding to the \( i \)th level of given \( J \) as

\[ \psi_i = \sum_m \sum_k \alpha_{m,k}^i |m, J, k, M\rangle \]  

(3-15)

and letting initial (primed) and final (unprimed) states be \( \psi_i = \sum_m \sum_k \alpha_{m,k}^i |m', J', k', M'\rangle \) and \( \psi_f = \sum_m \sum_k \alpha_{m,k}^f |m, J, k, M\rangle \), \( D_{i\rightarrow f} \) can be written as,

\[ D_{i\rightarrow f} = g_n \left( (2S+1)(2J+1)(2J'+1) \right) \times \]

\[ \left( \sum_{\ell=-1}^{1} \sum_{m'} \sum_m \sum_{k'} \sum_k \alpha_{m,k}^i \alpha_{m',k'}^f \langle m' | 0_{m',\ell} | m \rangle (-1)^{k'} \left( \begin{array}{ccc} J' & 1 & J \\ k' & \ell & -k \end{array} \right) \right)^2 \]  

(3-16)

Note that from the property of the 3-j symbol, only the cases in which \( |J' - J| = 0, 1 \) will have non-zero matrix elements.

Before going any further with EQ. (3-16), consider the electric dipole moment of CH\(_3\)NO\(_2\). Components of the dipole moment along molecule-fixed axes \( a, b \) and \( c \) are calculated from the equilibrium positions and effective charges of each atom given in Table (3-2). The Table (3-2) shows the calculated dipole moment along C – N axis to be 3.5 debye and a component of the dipole moment perpendicular to the C – N axis to be 0.05 debye\(^{16}\). By neglecting the small perpendicular component of the dipole moment, \( \ell = \pm 1 \) terms appearing in EQ. (3-16) can be neglected. When \( \ell = 0 \), 3-j symbol terms are non-vanishing only if \( k' = k \). In addition, since the torsional angle only affects positions
of the hydrogen atoms along $b$ and $c$ axes, $\mu_a$ is independent of the torsional angle (torsional mode $m$). Thus,

$$\langle m | \mu_{m,0} | m' \rangle = \mu_a \delta_{m,m'}, \quad (3-17)$$

and $D_{i\rightarrow f}$ is simplified to

$$D_{i\rightarrow f} = g_n (2S+1)(2J+1)(2J'+1) \mu_a \sum_m \sum_k \alpha_{m,k}^f \alpha_{m,k}^{j'} (-1)^k \begin{pmatrix} J' & 1 & J \\ k & 0 & -k \end{pmatrix}^2 \quad (3-18)$$

<table>
<thead>
<tr>
<th>Atom</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>Effective Charge (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>0.182</td>
<td>0</td>
<td>0</td>
<td>0.42</td>
</tr>
<tr>
<td>O</td>
<td>0.726</td>
<td>1.092</td>
<td>0</td>
<td>-0.31</td>
</tr>
<tr>
<td>O</td>
<td>0.726</td>
<td>-1.092</td>
<td>0</td>
<td>-0.31</td>
</tr>
<tr>
<td>C</td>
<td>-1.308</td>
<td>0</td>
<td>0</td>
<td>0.05</td>
</tr>
<tr>
<td>H</td>
<td>-1.672</td>
<td>0</td>
<td>-1.027</td>
<td>0.06</td>
</tr>
<tr>
<td>H</td>
<td>-1.672</td>
<td>0.890</td>
<td>0.514</td>
<td>0.05</td>
</tr>
<tr>
<td>H</td>
<td>-1.672</td>
<td>-0.890</td>
<td>0.514</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Dipole Moment $\mu$ 3.4 $D$ 0 0.05 $D$

a. REF. (16)

After solving the rotational-torsional levels, their eigenstates and $D_{i\rightarrow f}$, the line-integrated absorption coefficient $A_{i\rightarrow f}$ can be calculated from Eq (2-37). In order to calculate a precise absorption coefficient $\alpha(\nu)$, the line shape functions $W_{i\rightarrow f}$ must also be known. However, low resolution spectra can be calculated by using an instrumental line shape function instead of $W_{i\rightarrow f}$ as long as the width of the instrumental line shape function is much wider than the width of the actual line shape function.
In Chapter 6, the rotational-torsional energy levels, the transition frequencies and the line intensities of CH$_3$NO$_2$ will be calculated for the rotational quantum number $J$ from 1 to 120 and the torsional quantum number $m$ ranging from -20 to 20. The calculated spectrum was then convolved with an instrumental line function and compared with the experimental spectrum obtained by the FTIR.

### 3.3 Laser-induced IR emission spectrum

A molecule can be vibrationally excited by irradiating it with an infrared laser whose photon energy corresponds to the excitation energy. Following the laser excitation, the excited molecules will eventually decay to a thermal equilibrium state by either colliding with other molecules or emitting radiation. The process which transfers vibrational energy to other molecules is called vibrational energy transfer (VET). An excited molecule can collide with another excited molecule, further exciting to a higher state, or it can collide with an unexcited molecule which could be either the same or a different type of molecule. The VET process redistributes the laser-excited state and brings the whole system, including molecules which were not irradiated, to thermal equilibrium state in which the populated states can be described by a statistical temperature. Thus, the emission following the laser excitation is considered as thermal emission from molecules heated by the laser. Since the populated states after the initial laser excitation depend only on a statistical temperature, it is possible for states whose energy is well above the exciting laser energy to be populated. In fact, it will be shown in
Chapter 6 that when CH$_3$NO$_2$ is irradiated at 943 cm$^{-1}$ wavenumber, induced emissions were observed well above the laser wavenumber.

In addition to the thermal emission following laser excitation, there are also fluorescent emissions directly from a laser excited state. The intensity of the laser induced IR fluorescence strongly depends on the spontaneous emission rate (Einstein's A coefficient) and its quantum efficiency given by $\frac{A}{A+K}$ where $A$ is the Einstein's A coefficient and $K$ is the non-radiative relaxation rate which is proportional to pressure$^{28}$. Due to the well known $\nu^3$ dependency of $A$, the intensity of fluorescence in the IR frequencies is very weak compared to the visible-UV frequencies and the dominant relaxation process after the IR excitation is by collision. It has been reported that to observe IR fluorescence, the pressure must be below $10^{-4}$ mmHg in order to suppress the non-relaxation relaxation process such as collisions$^{28}$. Since a typical pressure of CH$_3$NO$_2$ in this work is about 10 mmHg, we do not expect to see any fluorescent spectrum. Consequently, the induced emission spectrum is expected to be thermal emission from laser heated CH$_3$NO$_2$ molecules.
Chapter 4
Experiment

4.1 Fourier Transform Spectrometer (FTIR)

In the experiment, a Bruker IFS 66v/S Fourier transform spectrometer (FTIR) was exclusively used to acquire various spectra. Thus, it will be helpful to review the Bruker IFS 66v/S spectrometer and how a FTIR works in general.

Simply put, a FTIR is nothing more than a Michelson interferometer. FIG. (4-1) shows schematic description of the Michelson interferometer. Broadband radiation from a source is directed to a beamsplitter. The beamsplitter ideally reflects 50% and transmits 50% of the incident light. Then, the split beams are reflected from fixed and movable mirrors. Since one of the mirrors is movable, when they recombine at the beam splitter, there can be an optical path difference $\delta$ between the two beams. Thus, intensity of a monochromatic light whose frequency is $\nu$ is given by

$$I_\nu(0) = \frac{1}{2} I_\nu(0)(1 + \cos 2\pi \nu \delta)$$  \hspace{1cm} (4-1)

Ignoring the constant term, when the source is broadband, the intensity measured at the detector as a function of $\delta$ is given by

$$I(\delta) = \int_{0}^{\infty} B(\nu) \cos(2\pi \nu \delta) d\nu$$  \hspace{1cm} (4-2)

which is called an interferogram, where $B(\nu)$ is a source spectrum modified by a sample transmission and instrumental losses which are due to the beamsplitter, mirrors, apertures, etc. By taking the ratio of spectrum with and without the sample, the absorption
spectrum is obtained. It is clear from Eq. (4-2) that \( I(\delta) \) and \( B(\tilde{\nu}) \) are Fourier transforms of each other.

Ideally, a FTIR spectrum is obtained by simply performing a Fourier transformation to a recorded interferogram.

\[
B(\tilde{\nu}) = \int_{-\infty}^{\infty} I(\delta) \exp(-i2\pi\tilde{\nu}\delta) d\delta
\]  

(4-3)

However, there are two physically imposed limitations on \( I(\delta) \). First, the measured \( I(\delta) \) is not continuous function and has a finite sampling interval. In order to avoid aliasing when performing a Fourier transformation, the sampling interval \( \Delta \delta \) must satisfy

Figure 4-1. Schematic representation of the Michelson interferometer
\[ \Delta \delta \leq \frac{1}{2} \lambda_{\text{min}} = \frac{1}{2 \bar{\nu}_{\text{max}}} \]  

(4-4)

where \( \bar{\nu}_{\text{max}} \) is the highest wavenumber (frequency) present in the spectrum. Most commercially available FTIRs including ours measure the optical path difference \( \delta \) by fringes of an internal HeNe laser which is co-aligned in the Michelson interferometer section of the instrument. So the FTIR can have a smallest sampling interval of 317 nm which is usually sufficient for the most FTIR applications since the high frequency part of a spectrum can be easily eliminated by either an optical or electronic filter. The other limitation is that it is mechanically impossible to record an interferogram extending to infinity. When the interferogram is truncated, the integration shown in EQ. (4-3) becomes

\[
B'(\bar{\nu}) = \frac{A}{2} \int I(\delta) \exp(-i2\pi \bar{\nu} \delta) d\delta
\]

or equivalently

\[
B'(\bar{\nu}) = \int I(\delta) \text{rect} \left( \frac{\delta}{\Delta} \right) \exp(-i2\pi \bar{\nu} \delta) d\delta
\]

(4-5)

where \( \Delta \) is the limit which the movable mirror can move. It is evident from EQ. (4-5) that the result of a Fourier transformation performed on an interferogram of a finite length will be a true spectrum convolved with a sinc function (Fourier transform of rect function).

\[
B'(\bar{\nu}) = \int B(\bar{\nu}') \text{sinc} \left[ \Delta(\bar{\nu} - \bar{\nu}') \right] d\nu'
\]

(4-6)
Since the sinc function exhibits large side lobes (~21% of peak), it is often not an ideal function to be convolved with especially when there are small absorption lines near a large line. Therefore, in most cases, the interferogram appearing in EQ. (4-5) is multiplied by a function which smoothly approaches zero at the limits of the interferogram rather than a sudden truncation. The process is called apodization and the spectrum obtained this way will be convolved with the Fourier transform of the apodization function instead of the sinc function. Apodizing an interferogram can diminish side lobes, however, at the expense of spectral resolution.

FIG. (4-2) and FIG. (4-3) shows a picture of the Bruker IFS 66v/S spectrometer and its schematic representation. IFS 66v/S spectrometer can be operated either purged or under vacuum. The capability to operate under vacuum offers a great advantage since it eliminates noisy absorption lines due to H₂O and CO₂ in the atmosphere. FIG. (4-4) shows sample background spectra while the FTIR is under vacuum and vented to atmosphere. The spectral range of IFS 66v/S is determined by choosing three main components, source, beamsplitter and detector. Table (4-1) provides components and their spectral range available to our IFS 66v/S spectrometer.
Figure 4-3. Schematic view of Bruker IFS 66v/S spectrometer

Figure 4-4. Source spectrum when the FTIR is placed under vacuum (top) and vented to atmosphere (bottom)
Table 4-1. Components and their spectral ranges available to IFS 66v/S spectrometer.

<table>
<thead>
<tr>
<th>Components</th>
<th>Spectral range cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source</td>
<td></td>
</tr>
<tr>
<td>Globar</td>
<td>12 ~ 7,500</td>
</tr>
<tr>
<td>Hg arc lamp</td>
<td>8 ~ 100</td>
</tr>
<tr>
<td>Beamsplitter</td>
<td>100 μm Mylar</td>
</tr>
<tr>
<td></td>
<td>8 ~ 27</td>
</tr>
<tr>
<td></td>
<td>6 μm multi-layer</td>
</tr>
<tr>
<td></td>
<td>12 ~ 700</td>
</tr>
<tr>
<td></td>
<td>KBr/Ge</td>
</tr>
<tr>
<td></td>
<td>650 ~ 7,500</td>
</tr>
<tr>
<td>Detector</td>
<td></td>
</tr>
<tr>
<td>Si Bolometer</td>
<td>&lt; 100</td>
</tr>
<tr>
<td>DLaTGS</td>
<td>12 ~ 700</td>
</tr>
<tr>
<td>MCT (HgCdTe)</td>
<td>550 ~ 7,500</td>
</tr>
</tbody>
</table>

4.2 Experiment Setup (THz spectrum of CH\(_3\)NO\(_2\))

THz spectrum of gaseous CH\(_3\)NO\(_2\) is obtained by the IFS 66v/S spectrometer equipped with a Globar source, a 6 μm multi-layer and a 100 μm beamsplitters, and a DLaTGS detector. The spectrum was taken with a 10 cm single pass gas cell fitted with two crystalline quartz windows which transmit well in the wavenumber below 200 cm\(^{-1}\). The gas cell completely fits in the sample compartment of the IFS 66v/S spectrometer. Prior to the experiment, the gas cell was thoroughly cleaned and placed under vacuum for at least 48 hours to eliminate any contamination. CH\(_3\)NO\(_2\) whose purity is greater than 99.0% was purchased from SIGMA-ALDRICH and used as received. Liquid CH\(_3\)NO\(_2\) was initially placed in the gas cell and the cell was evacuated. Then, liquid CH\(_3\)NO\(_2\) boils inside the cell until the equilibrium vapor pressure (~30 mmHg) is reached. The IFS 66v/S spectrometer is capable of performing with 0.25 cm\(^{-1}\) spectral resolution. However, the intensity of a Globar or a Hg arc lamp, being blackbody sources, is very
weak in the THz frequency range and in order to achieve a reasonable signal to noise ratio (S/N), the THz spectrum was recorded with 1 cm$^{-1}$ resolution.

4.3 Experiment Setup (laser induced IR emission of CH$_3$NO$_2$

FIG. (4-5) and (4-6) shows the experiment setup used to acquire CO$_2$ laser (10.6 μm wavelength) induced IR emission spectrum of CH$_3$NO$_2$. The external compartment next to the IFS 66v/S spectrometer is called PL module. Unlike the spectrometer, the PL module cannot be placed under vacuum and it is usually vented to the atmosphere. The wavelength of the CO$_2$ laser falls in the R-branch of the C-N stretch vibrational mode which is centered at 917 cm$^{-1}$. Liquid CH$_3$NO$_2$ was placed in the gas cell and vaporized in the cell as described in the previous section. This time, the gas cell was fitted with two AR coated ZnSe windows for the CO$_2$ laser to go through and a KBr window to let the IR emission come out. KBr is transparent from visible to 300 cm$^{-1}$ wavenumber. CH$_3$NO$_2$ vapor in the gas cell is irradiated with a C.W. CO$_2$ laser and emitted radiation is directed to the spectrometer as shown in FIG. (4-6). The solid angle of the collected emission is approximately 0.046 sr which is limited by the size of the KBr window. There is also a germanium coated KBr window at the side of the FTIR where the emission enters. When acquiring a spectrum in the IR region, the KBr beamsplitter and the liquid N$_2$ cooled MCT detector were used in the IFS 66v/S spectrometer.
Figure 4-5. Setup used to acquire CO$_2$ laser induced IR emission spectrum of CH$_3$NO$_2$. 
Figure 4-6. Picture of the PL module.

The CO$_2$ laser used in this experiment (Merit by Access Laser Inc.) has a nearly Gaussian profile ($M^2 < 1.2$) and the power density at the focal point of the collecting mirror [parabolic mirror next to the gas cell in FIG. (4-6)] was determined by measuring a beam radius using an adjustable vertical slit. While one side of the slit is always fixed (at $x = 0$), the intensities of the laser transmitted through the slit was measured by a Gentec-EO QE25SP power meter as the other side of the slit is moved. The intensities recorded at different slit widths are fitted with the function given by

$$P(x) = \frac{P_0}{w} \sqrt{\frac{2}{\pi}} \int_0^x \exp \left[ -\frac{2(x' - x_0)^2}{w^2} \right] dx'$$

(4-7)
where \( P_0 \), \( w \), and \( x_0 \) are total power, beam radius and center of the beam measured from the fixed side of the slit. FIG. (4-7) shows the CO\(_2\) laser power as a function of the slit widths and the result of fitting EQ. (4-7). Using the power and radius obtained from the fit, power density at the center of the beam is determined to be 19.2 W/cm\(^2\).

![Graph showing measured and fitted CO\(_2\) laser power](image)

**Figure 4-7.** Measured CO\(_2\) laser power and the result of the fit using EQ. (5-7). The error associated with \( P_0 \) comes from calibration uncertainty of the power meter.

In addition to analyzing the laser-induced IR emission spectrum, the decay constant of the emission was measured with a Coherent P4 pyroelectric detector. FIG. (4-8) shows the experiment setup used to measure the decay constant. CH\(_3\)NO\(_2\) was vaporized in the evacuation chamber. After evacuating the emission cell, the cell was
filled with CH$_3$NO$_2$ gas. This time, the CO$_2$ laser was pulsed at 100 ms and the emission was directly measured without the FTIR. Thus, the decay constant measured can not be attributed to any particular emission line or band and it should only be regarded as an overall average decay constant.

![Diagram of setup used to measure the decay constant of CO$_2$ laser induced IR emission.](image)

**Figure 4-8** Setup used to measure the decay constant of CO$_2$ laser induced IR emission.

In principle, a pyroelectric detector responds to a relative change in the detector element's temperature and has relatively long decay constant (~ 0.1 s) which is
comparable to a decay constant of an IR emission. Thus, in order to extract a decay constant of the IR emission, the detector output must be deconvoluted with the detector's response function. A detector output \( G(t) \) in response to an IR emission \( S(t) \) is given by

\[
G(t) = \int_{-\infty}^{t} S(\tau) R(t-\tau) \, d\tau
\]

(4-8)

where \( R(t) \) is the detector's response function. Since obviously the detector cannot respond before the signal (i.e. \( R(t) = 0 \) for \( t < 0 \)), the upper limit of the integration in EQ. (4-8) can be extended to infinity

\[
G(t) = \int_{-\infty}^{\infty} S(\tau) R(t-\tau) \, d\tau
\]

(4-9)

Then, the standard deconvolution can be carried out in the frequency domain

\[
\tilde{S}(\omega) = \frac{\tilde{G}(\omega)}{\tilde{R}(\omega)}
\]

(4-10)

and \( S(t) \) is recovered by simply taking inverse Fourier transform of \( \tilde{S}(\omega) \). The response function \( R(t) \) was experimentally obtained by recording a response to the short (40 \( \mu \)s) CO\textsubscript{2} laser pulse and shown in FIG (4-9).
Figure 4-9. The P4 pyroelectric detector's response (top) to a 40 μs CO₂ laser pulse (bottom). The CO₂ laser pulse was measured by a fast photoelectromagnetic (PEM) HgCdZnTe detector.
Chapter 5
Results and discussion

5.1 THz spectrum of CH$_3$NO$_2$

FIG. (5-1) shows experimental and calculated THz absorption spectrum of CH$_3$NO$_2$. The THz spectrum was recorded with 1 cm$^{-1}$ resolution. In the measured spectrum, the peak of rotational-torsional band is seen at 23 cm$^{-1}$. A series of sharp lines appearing in wavenumber above 40 cm$^{-1}$ are due to H$_2$O likely from the impurity in the sample and the residual air in the gas cell. The absorption spectrum of distilled water is provided in FIG. (5-2) for comparison.

The energy levels, dipole transition moments and absorption coefficients of CH$_3$NO$_2$ were calculated according to Chapter 3. In calculating the energy levels and eigenstates, recalling that the Hamiltonian matrix is block diagonal in sets of torsional quantum number $m$ differing by six, the Hamiltonian matrices which include following sets of $m$ were constructed and diagonalized in $|m, J, k\rangle$ basis for $J$ up to 120

Set 1. $m = -18, -12, -6, 0, 6, 12, 18$
Set 2. $m = -17, -11, -5, 1, 7, 13, 19$
Set 3. $m = -19, -13, -7, -1, 5, 11, 17$
Set 4. $m = -16, -10, -4, 2, 8, 14, 20$
Set 5. $m = -20, -14, -8, -2, 4, 10, 16$
Set 6. $m = -21, -15, -9, -3, 3, 9, 15, 21$
Setting the cut-off intensity to 0.3% of the strongest transition, the calculation yielded over 100,000 transitions lines. Since it is clearly impractical to list these lines in the form of table, a histogram is provided in FIG. (5-3).

Figure 5-1. Measured (black) and calculated (red) THz spectrum of CH3NO2.
Figure 5-2. THz spectrum of CH$_3$NO$_2$ (top) and distilled water (bottom).

Figure 5-3. Calculated rotational-torsional transitions at 300K.
The calculated absorption coefficients were then convoluted with the instrumental line shape function (Gaussian with $FWHM = 1 \text{ cm}^{-1}$). As it is seen in FIG. (5-1), the peak of the calculated rotational-torsional band is located at 14 cm$^{-1}$. There may be a number of factors which contribute to the discrepancy between the observed and calculated spectra. For example, all the rotational constants given in Table (3-1) are based on rotational-torsional transitions in the microwave region which involve states with only small $J$ values, whereas our calculation showed that the dominant transitions at room temperature typically involve $J$ ranging from 10 to 30 and $m$ ranging from −4 to 4.

Therefore, inaccuracies in the rotational constants will be especially pronounced for the terms which vary as $J^4$ in the Hamiltonian. In addition, omission of higher order terms such as those that vary as $J^6$ may have contributed to the discrepancy particularly for the energies of high $J$ states. To see if the fit could be improved, additional symmetry breaking Hamiltonian matrix elements reported by Sorensen, et al. are added to the original Hamiltonian given in EQ. (3-6) through (3-9)$^{14}$

\[
\begin{align*}
\langle m, J, k | R_6 | m+3, J, k \pm 1 \rangle &= \frac{m}{4} (k_b \pm k_c) \sqrt{J(J+1) - k(k \pm 1)} \\
\langle m, J, k | R_6 | m+6, J, k \rangle &= \frac{1}{2} [b_6 J(J+1) + b_3 k^2] \\
\langle m, J, k | R_6 | m+6, J, k \pm 2 \rangle &= \frac{1}{4} b_6 \sqrt{J(J+1) - (k \pm 2)(k \pm 1)} \sqrt{J(J+1) - k(k \pm 1)}
\end{align*}
\]
Table 5-1. Coefficients appearing in EQ. (5-1) (cm$^{-1}$)

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b_{jj}$</td>
<td>-1.76289 × 10^{-5}</td>
</tr>
<tr>
<td>$b_{zz}$</td>
<td>6.34 × 10^{-4}</td>
</tr>
<tr>
<td>$b_{B}$</td>
<td>-3.6792 × 10^{-6}</td>
</tr>
<tr>
<td>$k_b$</td>
<td>4.08449 × 10^{-2}</td>
</tr>
<tr>
<td>$k_c$</td>
<td>-4.343 × 10^{-3}</td>
</tr>
</tbody>
</table>

However, while some shifts in transition frequencies were observed as a result of additional terms in EQ. (5-1), these changes were too small to be observed after convolving with the instrumental line shape function.

Nonetheless, the cause of the discrepancy whether it is due to the model, the values of rotational coefficients or the instrumental errors could not be determined with the spectral resolution set for this experiment. A typical line spacing of CH$_3$NO$_2$ spectrum in the THz frequency range is less than 10 MHz and acquisition of such a high resolution spectrum requires an extremely narrowband light source such as a tunable THz free electron laser.

In addition to the possible discrepancies in the constants used in the calculation, the possibility of instrumental error should not be neglected. While an FTIR is an excellent spectroscopic instrument because of its wide frequency range, the performance in the THz frequency is marginal at best due to the source. An FTIR uses a blackbody such as Globar and Hg arc lamp for its radiation source. However, the blackbody radiation is extremely weak in the THz frequency range. Therefore, it is possible that the intensity of the source in the THz frequencies is near or below the threshold power of the detector. If this is the case, the detector’s response may not be linear causing the peak to shift.
5.2 CO₂ laser induced IR emission spectrum

FIG. (5-4) shows the steady state CW CO₂ laser (~19 W/cm²) induced IR emission spectrum obtained with the FTIR. Unfortunately, the attenuation property of the FTIR (i.e. beamsplitter, detector window, mirrors, etc.) is not known and can not be measured accurately without a calibrated blackbody source. Hence, one must keep in mind that the spectrum presented in this section is uncorrected for such losses. The three intense lines seen near 943 cm⁻¹ (10.6 µm) in FIG. (5-4) are from the CO₂ laser. These lines corresponds to some of the lasing transitions of the CO₂ laser [10P20 (944.2 cm⁻¹), 10P24 (940.5 cm⁻¹), 10P28 (934.9 cm⁻¹)]. The sharp absorption lines appearing in the spectral region 1,350 cm⁻¹ ~ 1,600 cm⁻¹ and near 670 cm⁻¹ are due to H₂O and CO₂ in the atmosphere. By purging the PL module with N₂, these lines can be minimized as shown in FIG. (5-5). Also, re-absorption of emitted radiation by CH₃N0₂ itself is seen at 1583 cm⁻¹ where the strongest IR absorption band of CH₃NO₂ is located.

The emission spectrum has a strong resemblance to the absorption spectrum provided in FIG. (5-6), except where strong absorptions are causing the re-absorption of emitted radiation. In addition to the emission from the laser-excited band, emissions were observed from both below and above the laser-excited band. This is consistent with the assumption that the observed emission is from a laser-heated thermal equilibrium state as discussed in Section 3.3. Compared to the absorption spectrum, the relative intensity of emission bands located near 1,500 cm⁻¹ is quite small compared with other emission bands and in addition, no emission was observed above 1,800 cm⁻¹. This is also consistent with thermal emission since the emission intensity diminishes as the frequency
is increased according to the blackbody emission curve. In theory, it is possible to determine the statistical temperature of the laser-heated state. However, without knowing the attenuation loss of the measuring system, the statistical temperature of the gas could not be determined. To determine whether CH$_3$NO$_2$ was decomposed as a result of the CO$_2$ laser irradiation, IR transmission spectra were recorded before and after the 30 minutes CW CO$_2$ laser irradiation and there were no differences between the spectra.

![IR emission spectrum of CH$_3$NO$_2$](image)

Figure 5-4. C.W. CO$_2$ laser induced IR emission spectrum of CH$_3$NO$_2$
Figure 5-5. C.W. CO₂ laser induced IR emission spectrum of CH₃NO₂ with PL module purged with N₂.

Figure 5-6. IR absorption spectrum of CH₃NO₂ (T = 25 °C).
FIG. (5-7) shows an example of the original and deconvolved pyroelectric detector output in the experiment whose setup is shown in FIG. (4-8). The IR emission induced by a 100 ms CO2 laser pulse is seen in the deconvolved signal and the exponential decay was fitted in red. FIG. (5-8) shows deconvoluted laser induced IR emission signals at various pressure and FIG. (5-9) shows decay constants of the IR emission and intensities immediately after the CO2 laser pulse at different pressures. The low pressure limit of the experiment was imposed by the range of the pressure gauge used. As the pressure is increased beyond 15 mmHg, the decrease in the emission intensity was observed. This could be attributed to the fact that the collisional decay process starts to dominate as the pressure increases. Due to small IR emission signals, decay constants could not be determined for the pressures above 15 mmHg. The emitted powers shown in FIG. (5-8) and FIG. (5-9) were determined by calibrating the pyroelectric detector against the QE25SP (Gentec-eo) laser power meter which was calibrated by the manufacture in 2005. The size of the pyroelectric detector element is 4 mm x 4 mm, and the solid angle subtended from the center of the gas cell to the detector was 0.055 srad.

For a remote sensing application, it will be useful to estimate the power emitted per molecule per unit solid angle. From the geometries and sizes of the gas cell, the window, the detector, and the laser profile, a volume of CH3NO2 gas which is visible from the detector was determined to be 3.28 cm³. For simplicity, it is assumed that the solid angle subtended from any parts of this volume to the detector to be 0.055 srad. This is a reasonable assumption considering that the detector is 4 mm wide and the distance between the detector and the center of the gas cell is 60.3 mm. Using the ideal gas law
\[ N = \frac{PV}{k_B T}, \] the number of molecules in the volume visible from the detector is estimated to be \(3 \times 10^{18}\) (13 mmHg pressure). So for example, at 13 mmHg pressure, FIG (5-8) shows the emitted power following a CO\(_2\) laser pulse (100 ms at 19 W cm\(^{-2}\)) to be 20 \(\mu\)W. Using the number of molecules and the solid angle above, the emission following the laser-irradiation in this case is calculated to be \(\sim 10^{-22}\) W/srad/molecule. Note that this is an order of magnitude approximation for this particular case and integrated over frequencies. In order to accurately quantify the result, more careful geometrical analysis must be performed and any effects caused by non-uniform laser illumination within the volume must be carefully analyzed.

In addition to the measurements made by the pyroelectric detector, series of low resolution FTIR spectra was recorded during and after the CO\(_2\) laser irradiation and the result is shown in FIG (5-10). The time required to take single spectrum depends on spectral resolution (the distance the movable mirror must travel) and the velocity of the mirror. In this particular case, it was approximately 10 ms. Since the FTIR does not have the capability to record a time resolved spectrum, time between each spectrum is unknown. However, it is seen that all emission bands have relatively same decay constant.

To determine if the laser-induced emission can be observed without vaporizing the gas cell, an emission spectrum of CH\(_3\)NO\(_2\) in the ambient atmospheric condition was recorded and shown in FIG (5-11). In obtaining the spectrum in FIG. (5-11), liquid CH\(_3\)NO\(_2\) was simply placed 3.5 cm below the CO\(_2\) laser beam in the atmospheric condition. Since there is still substantial emission at the atmospheric condition, the
possibility of using the laser induced IR emission as a remote sensing tool for detecting the CH$_3$NO$_2$ should be carefully explored.

Figure 5-7. Response of the pyroelectric detector to the CO$_2$ laser induced (100 ms pulse) IR emission (bottom) and its deconvoluted signal (top).
Figure 5-8. Deconvoluted detector signal of the CO₂ laser induced IR emission at various pressure.

Figure 5-9. Emission intensity and decay constant of the CO₂ laser induced IR emission obtained from results of exponential decay fit performed on deconvoluted pyroelectric detector signals.
Figure 5-10. Low resolution (6 cm\(^{-1}\)) CO\(_2\) laser induced IR emission spectra of CH\(_3\)NO\(_2\) during (black) and after (red/blue) the laser irradiation.

Figure 5-11. CO\(_2\) laser induced IR emission spectrum of CH\(_3\)NO\(_2\) vapor in atmosphere (black). The emission spectrum of vaporized CH\(_3\)NO\(_2\) (red) is provided for comparison.
PART II

Optical properties of laser-induced carriers on semiconductor surfaces probed by a 10.6 μm CO$_2$ laser
Chapter 6
Introduction

As it was mentioned in Part I of this study, the trend in the number of research publications using THz radiation has been steadily rising for the past decade. Clearly, the availability of intense and narrowband THz radiation sources is important in advancing THz technology. However, most THz sources currently commercially available such as blackbody, backward wave oscillator and Auston emitter are neither intense nor narrowband. Typically these sources only produce power ranging from nW to a few W in the THz frequency range. One exception is the CO2 laser pumped molecular laser which can generate narrowband THz radiation with power up to a few hundred W. However, molecular lasers can only lase at discrete frequencies determined by the medium. Other laser technologies currently being developed such as quantum cascade lasers (QCL) and parametric oscillators (OPO) are more tunable than the molecular laser; however their power output is less than that of a molecular laser.

Currently, accelerator-driven systems such as FEL and synchrotron light sources are the only devices that can deliver intense and narrowband THz radiation. For example, as mentioned in Chapter 1, UH THz FEL can generate high power (~ kW) quasi-C.W (~ µs pulse width) continuously tunable (0.38 ~ 1.2 THz) THz radiation with very narrow bandwidth (∆ω/ω ~ 10⁻⁸). One of the improvements planned for the UH THz FEL before the recommissioning of the FEL was put on indefinite hold was to provide an option to shorten the pulse length and increase the peak power. Pulsed intense THz
radiation is ideal for applications such as imaging, non-linear optics, time-resolved spectroscopy, radar etc.

In order to generate short THz pulses, a fast optical switch may be required. However, unlike the visible or IR region of the spectrum, fast electro-optical devices such as Q-switch are not available in the THz frequency range. One solution to this problem is to use a laser-activated semiconductor switch.

When a semiconductor is irradiated with a laser whose photon energy is greater than the band gap energy, a large number of electron-hole (e-h) pairs (carriers) are generated on the surface. As a result, the semiconductor’s surface becomes opaque to the THz radiation for the duration determined by either the pulse width of the incident laser or the lifetime of carriers whichever is longer. The detail of this process will be discussed in the next chapter.

One way to shorten the FEL pulse width is to incorporate a laser-activated semiconductor switch into a cavity dump mechanism. FIG. (6-1) shows a schematic description of such cavity dump system. The cavity can be either the FEL resonant cavity or an external cavity fed by the FEL output. In either case, linearly polarized THz radiation is stored in the cavity and a semiconductor plate (switch) is placed at the Brewster angle. When the saturation in the cavity is reached, the switch is activated by the external laser and the radiation stored is reflected out of the cavity.

There are several advantages in using a cavity dump switch coupled at the Brewster angle. First, higher output power is achieved by using a cavity dump switch compared to a conventional output coupler. In the cavity dump system, the entire power stored in the cavity can be extracted while only a fraction of the power is extracted with
the output coupler. In addition, the power within the cavity itself becomes higher since the output coupler is replaced with a Brewster plate reducing the cavity loss. Second, the change in a refractive index is minimal in the THz frequency range. Thus, the same Brewster's angle can be used in the entire tunable range of the FEL. For example, silicon's refractive index is 3.4155 at 1 THz and 3.4185 at 3.3 THz\textsuperscript{29}. A simple calculation will show that added reflection loss due to the shift in refractive index is less than $10^{-7}$. Third, by placing a cavity dump switch at the Brewster's angle, the damage threshold of the switch can be improved because of the increased cross section of the THz radiation beam stored in the cavity.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{cavity_dump.png}
\caption{Schematic description of cavity dump mechanism using a laser-activated semiconductor switch.}
\end{figure}

The long-term goal of this study is to find the best combination of material and laser to be used for the cavity dump switch. Important deciding factors for determining the preferred combination are laser-induced reflectance, duration of the activated switch, attenuation property in the THz frequency range, and the damage threshold.
Initially, a laser activated semiconductor switch was used to generate short mid-infrared CO$_2$ laser pulses by a pulse slicing technique$^{30-32}$. Since then, the same technique also has been applied in the THz frequency range in recent years$^{33-39}$. The use of a laser activated semiconductor switch as an FEL cavity dump switch was first demonstrated by Kaminski et al who used a high purity Si wafer in the resonant cavity of the UC Santa Barbara’s FEL to generate 37 ns THz radiation pulses at 1.5 THz with a peak power of 7.3 kW$^{40}$. Using the same FEL, Burghoorn et al. were able to generate 400 ps pulses at 2.5 THz with a peak power of 11 kW by incorporating a laser-activated high purity Si switch into a passive cavity fed by the FEL$^{41}$. In addition to the switching of optical pulses, the laser-irradiated semiconductors are often probed by a visible and infrared laser to study the dynamics of induced carriers$^{42-51}$.

The materials studied in the past as optical switches are almost exclusively high resistivity single crystal semiconductors. In this study, instead of single crystal semiconductors, several polycrystalline semiconductors will be evaluated for their laser-induced changes in optical properties. The reason which polycrystalline materials were chosen is because they have not extensively studied in past and also they are expected to have better time response due to the defects associated with a polycrystalline structure.

As it will be described in the next chapter, the dynamics of carrier density and consequently the optical property strongly depend on properties of materials such as intrinsic carrier density, carrier recombination rate, and surface recombination velocity which are highly dependent on sample specific parameters [$i.e.$ dopant concentrations, crystalline structure (single, poly, amorphous), surface condition (polished, etched)].
Therefore, it is necessary to develop a method to experimentally determine the optical properties of the laser-induced plasma in the THz frequency range.

Since the UH THz FEL is yet to be commissioned and its future uncertain, preliminary experiments were conducted using a CO₂ laser as a practice run for when or if the UH THz FEL becomes available. In this work, polycrystalline silicon (Si), germanium (Ge), gallium arsenide (GaAs) and cadmium telluride (CdTe) were irradiated with 150 ps 532 nm and 1064 nm wavelength Nd:YAG laser pulses and changes in the optical properties (reflectance and transmittance) were monitored by measuring the reflectance and transmittance of a CO₂ laser (10.6 μm) incident on samples oriented at the Brewster angle. These samples are typical IR window grade and their exact purity, dopant concentration, and resistivity could not be traced through vendors.
Chapter 7
Laser-induced carrier dynamics of a semiconductor

7.1 Carrier dynamic

When a semiconductor is irradiated with short laser pulses whose photon energy exceeds the band gap energy, a large number of carriers (e-h pairs) are created within a volume determined by the beam size and the penetration depth of the incident laser. As the number of carrier increases, its optical property becomes closer to that of metal characterized by strong absorption and high reflectance and the metal-like property which becomes more pronounced at lower frequencies.

In considering the carrier dynamics, it is important to define the time scale of interest. When an e-h pair is generated by absorbing a photon whose energy is $\hbar\omega$, the pair initially will have an excess energy $\hbar\omega - E_g - 3k_B T$ where $E_g$ is the band gap of the semiconductor and $3k_B T$ is the thermal kinetic energy of the pair $(2\times\frac{3}{2}k_B T')$. In the sub-picosecond time scale, excited carriers quickly thermalize via carrier-carrier interactions to a state described by the Fermi-Dirac distribution with a common carrier temperature

$$F(E) = \frac{1}{e^{\frac{E-E_{F,e,h}}{k_B T_c}} + 1}$$

(7-1)

where $E_{F,e,h}$ is the Fermi level of electrons (holes)\(^47\).

Initially, carrier temperature $T_c$ can be substantially higher than lattice (bulk) temperature depending on the laser photon energy and the band gap energy. However, in
the sub-nanosecond time scale, the carrier temperature and the lattice temperature reach equilibrium as the carriers interact with longitudinal-optical phonons in the lattice\textsuperscript{47}. In this study, the semiconductors were irradiated with 150 ps laser pulses and the induced changes in reflectance and transmittance were measured in the nanosecond time scale, limited by the time constant of a detector and the bandwidth of electronics. Therefore, when considering carrier dynamics in this time scale, carrier and lattice temperatures are indistinguishable.

A one-dimensional model describing the laser-excited carrier density in the limit of equal lattice and carrier temperatures was developed by Gallant and van Driel and summarized below\textsuperscript{43, 47}.

The carrier density \( N \text{ (cm}^{-3} \text{) within a semiconductor is determined by solving the continuity equation}

\[
\frac{\partial N}{\partial t} = -\nabla \cdot \mathbf{J} + G - R \tag{7-2}
\]

where \( \mathbf{J} \) is a current density, \( G \) and \( R \) are generation and recombination rates of carriers.

In the case of non-degenerate carrier distributions (i.e. \( E_c - \eta_e \ll kT, -E_v + \eta_h \ll kT \) where \( E_c \) and \( E_v \) are conduction and valance band edges), the current density is given by\textsuperscript{47}

\[
\mathbf{J} = -D \left( \nabla N + \frac{2N}{T} \nabla E_g + \frac{N}{2T} \nabla T \right) \tag{7-3}
\]

where \( D \) is the ambipolar diffusion coefficient. The first term represents the diffusion term, the second term represents the force fields arising from a spatial variation in the band structure due to the varying carrier density and the temperature, and the third term
represents the force field due to thermoelectric (Seebeck) effect. The carrier generation rate $G$ due to the absorption of laser energy is given by

$$G(z) = \frac{(1 - \Gamma) \alpha I(z, t)}{\hbar \omega} + \frac{(1 - \Gamma)^2 \beta I^2(z, t)}{2 \hbar \omega} \quad (7-4)$$

where $\Gamma$ is the reflection loss at the surface, $I(z, t)$ is the power of the laser in the semiconductor, $\alpha$ is the interband absorption coefficient and $\beta$ is the two-photon absorption coefficient. If the laser photon energy $\hbar \omega$ is well above (by a few factors) the band gap energy $E_g$, the two-photon absorption probability is typically negligible and also the conversion rate between absorbed photons and e-h pairs generated is near unity.

When this is the case, $I(z, t)$ will take the usual form

$$I(z, t) = I(t) \exp(-\alpha z) \quad (7-5)$$

However, when $\hbar \omega = E_g$, two-photon absorption and free carrier absorption processes may no longer be negligible. In the two-photon absorption process, an e-h pair is generated by absorbing two photons instead of one and in the free carrier absorption process, a free carrier gains kinetic energy by absorbing a photon which is eventually converted to the lattice heat. Hence in this case, $I(z, t)$ must satisfy

$$\frac{\partial I}{\partial z} = -\alpha I - \beta I^2 - \Theta NI \quad (7-6)$$

where $\Theta$ is a free carrier absorption coefficient and $N$ is a carrier density.

As the laser-induced carriers recombine, there are three recombination processes which can take place: Auger ($r_3$), radiative ($r_2$), and Shockley-Reed-Hall (SRH) ($r_1$) recombinations. After summing all three processes the total recombination rate appearing in EQ. (7-3) is given by
In the Auger recombination, the recombination energy of an e-h pair is absorbed by a third carrier. Since the Auger recombination involves three carriers, the recombination rate is proportional to $N^3$. Auger recombination is the dominant recombination process at high carrier density. In the radiative recombination process, the recombination energy is emitted in the form of a photon of energy $E_g$. Since this process involves single pair (two carriers), the recombination rate is proportional to $N^2$. The strength of the radiative recombination strongly depends on whether the material is a direct-gap or indirect-gap semiconductor. A direct-gap semiconductor has same crystal momentum at the bottom of conduction band and at the top of valance band while an indirect-gap semiconductor has different crystal momentum at conduction band minima and valance band maxima.

During the radiative recombination, an indirect-gap semiconductor requires a phonon to conserve both energy and momentum because of the offset in the crystal momentum.

The process can be described as

$$e(E_c, k_0) + h(E_v, k_0) \rightarrow \gamma(E_g) \quad \text{Direct-gap}$$

$$e(E_c, k_0 + \Delta k) + h(E_v, k_0) + \rho(\hbar c \Delta k) \rightarrow \gamma(E_g) \quad \text{Indirect-gap}$$

where $\gamma$ and $\rho$ are a photon and a phonon. Since the radiative recombination process of direct-gap semiconductor does not require a phonon, the radiative recombination rate of a direct-gap semiconductor is typically much greater than the rate of an indirect semiconductor. Lastly, during a SRH recombination, carriers decay by transitioning through impurity levels and energy lost at each transition is absorbed in the lattice. SRH
recombination rate is strongly affected by the purity and dopant concentration of a sample.

Because of the temperature dependence in EQ. (7-3), thus subsequently EQ. (7-2) and EQ. (7-6), the equation of carrier density must be coupled with the following lattice temperature equation\(^{43}\)

\[
\frac{\partial T}{\partial t} = \nabla \cdot (D_L \nabla T) + \frac{(1 - \Gamma) \alpha I(z, t)}{h \omega C_L} \left( \hbar \omega - E_g - 3k_BT \right) + \frac{R(E_g + 3k_BT)}{C_L} \tag{7-8}
\]

where \(D_L\) and \(C_L\) are thermal diffusion coefficient and specific heat of the lattice. The first term in EQ. (7-8) is the usual diffusion term, the second term represents the heat produced as laser-generated e-h pairs lose excess energy to the lattice, and the last term represents the heat produced when carriers recombine. This equation is only appropriate when the excess energy of e-h pairs is immediately lost to the lattice (i.e. nanosecond timescale).

The boundary conditions for coupled differential equations EQ. (7-2), EQ. (7-6), and EQ. (7-8) must account for the surface effect and given by\(^{43}\)

\[
N(L, t) = N_i \tag{7-9}
\]

\[
D \frac{\partial N(0, t)}{\partial z} = S \left[ N(0, t) - N_i \right] \tag{7-10}
\]

\[
I(L, t) = 0 \tag{7-11}
\]

\[
T(L, t) = 300K \tag{7-12}
\]

\[
\kappa_L \frac{\partial T(0, t)}{\partial z} + S \left[ N(0, t) - N_i \right] = 0 \tag{7-13}
\]

72
where \( N_i \) is the intrinsic carrier density, \( S \) is the surface recombination velocity and \( \kappa_L \) is the lattice thermal conductivity. The above boundary conditions assumes that the sample thickness \( L \) is sufficiently larger than the penetration depth of the incident laser (i.e. \( L \gg \alpha^{-1} \)).

### 7.2 Reflectance and transmittance

It may be surprising that numerous authors have implicated and shown that the optical properties of laser-excited semiconductor surface can be explained by a rather simple Drude model to a good approximation\(^{43, 47, 50, 51}\). The complex dielectric constant based on the Drude model is given by

\[
\epsilon_\omega = \epsilon_\infty + \frac{4\pi e^2 N}{m^* \omega} \frac{\tau}{1 - i \omega \tau} \quad \text{(cgs)}
\]  

(7-14)

and the complex refractive index is

\[
n_\omega = \sqrt{\epsilon}
\]

(7-15)

where \( \epsilon_\infty \) is the DC dielectric constant, \( m^* \) is the effective mass, and \( \tau \) is the relaxation time.

The dielectric constant of a laser-excited semiconductor is no longer homogeneous because the carrier density is not homogeneous. Optical properties of a one-dimensionally inhomogeneous material are calculated by the matrix method used for a stratified media whose each layer has thickness much less than the wavelength at which the optical properties are evaluated. This method is found in many standard optics text books and is briefly explained below\(^{52}\).
Consider the electric and magnetic field amplitudes at the boundaries of a homogeneous medium of thickness \( \delta z \). Defining the field amplitude vector \( U = \begin{bmatrix} E(z) \\ H(z) \end{bmatrix} \), for TE wave \( U = \begin{bmatrix} H(z) \\ E(z) \end{bmatrix} \) for TM wave, the amplitudes of fields at boundaries can be expressed as

\[
U(z) = MU(z + \delta z)
\]

(7-16)

where \( M \) is the characteristic matrix of a homogeneous medium of thickness \( \delta z \) whose components are given by

\[
M = \begin{bmatrix}
\cos(k_0 n \delta z \cos \theta) & -i \frac{\sin(k_0 n \delta z \cos \theta)}{p} \\
-i p \sin(k_0 n \delta z \cos \theta) & \cos(k_0 n \delta z \cos \theta)
\end{bmatrix}
\]

(7-17)

\[
p = \sqrt{\frac{\varepsilon}{\mu}} \cos \theta \quad \text{(TE wave)}
\]

(7-18)

\[
p = \sqrt{\frac{\mu}{\varepsilon}} \cos \theta \quad \text{(TM wave)}
\]

(7-19)

and \( \theta \) is the angle of incidence at the boundary. If the medium is composed of \( \ell \) homogeneous layers, then directly from EQ. (7-16)

\[
U(0) = \underbrace{M_1 M_2 M_3 \cdots M_\ell}_{\hat{M}} U(z_\ell)
\]

(7-20)

Let \( A_i \), \( A_r \) and \( A_t \) be the incident, reflected and transmitted amplitudes of the TE wave electric fields or the TM wave magnetic fields. Then in terms of \( A_i \), \( A_r \) and \( A_t \),

74
\[ U(0) = \begin{bmatrix} A_i + A_r \\ p_0 (A_i - A_r) \end{bmatrix} \]  

(7-21)

\[ U(z_s) = \begin{bmatrix} A_i \\ p^*_2 A_i \end{bmatrix} \]

It can be easily shown that the reflected and transmitted amplitude given in terms of matrix elements of \( M \) are

\[ r = \frac{A_r}{A_i} = \frac{(m_{11} + m_{22} p_t) p_0 - (m_{21} + m_{22} p_t)}{(m_{11} + m_{22} p_t) p_0 + (m_{21} + m_{22} p_t)} \]  

(7-22)

\[ t = \frac{A_t}{A_i} = \frac{2p_0}{(m_{11} + m_{22} p_t) p_0 + (m_{21} + m_{22} p_t)} \]  

(7-23)

and reflectance and transmittance are given by

\[ R = |r|^2 \]  

(7-24)

\[ T = \frac{P_t}{P_0} |t|^2 \]  

(7-25)
Chapter 8
Experiment

FIG. (8-1) shows the schematic description of the experiment setup. A frequency doubled (532 nm) or fundamental (1064 nm) wavelength 150 ps pulse width Nd:YAG laser (SL212P by Ekspla) is incident on a sample at near normal incidence (~ 1°). The SL212P laser is a Q-switched, diffraction limited laser which utilizes stimulated Brillouin scattering (SBS) cell for pulse compression. A diffuser (sand blasted glass) is placed in front of the sample so that the large area can be uniformly irradiated by the Nd:YAG laser. The maximum pulse energy of the SL212P is 200 mJ/pulse. However, due to a large scattering loss by the diffuser, the maximum fluence obtained was less than 30 mJ/cm² for 532 nm and 60 mJ/cm² for 1064 nm. FIG. (8-2) shows the calibration curve of laser fluence at the sample location through the diffuser with different laser amplification settings. The fluences were measured at the exact location where the Nd:YAG laser and the CO₂ laser overlaps on a sample and by using a 5.654 mm diameter aperture. For the duration of the experiment, several calibration curves were recorded and no significant shifts were observed.

A pulsed (250 μs), 10W, horizontally polarized CO₂ laser (Merit by Access Laser) is incident on the sample at the respective Brewster’s angles (74° for Si, 76° for Ge, 73° for GaAs, and 70° for CdTe). A HeNe laser is provided for alignment purpose. The residual reflectance measured at the Brewster’s angle was less than 3% for all samples. The diameter of the CO₂ laser was measured as described in Chapter 4 and determined to be 2 mm at the sample location.
The CO$_2$ laser pulse was monitored with a fast room temperature HgCdZnTe photoelectromagnetic (PEM) detector (PEM-L by Vigo) and a fast (1 GHz) pre-amplifier (also provided by Vigo). The spectral range of the detector is 2 ~ 12 μm and the rise time is less than 1 ns. A Ge filter was placed in front of the detector to shield the detector from scattered Nd:YAG laser pulses. As seen in FIG. (8-3), a PEM detector consists of a detector element and a set of permanent magnets. When the light is incident on the element, e-h pairs are generated near the surface. Since there is no bias voltage, the created e-h pairs diffuse towards back of the element. However, the magnetic field from the permanent magnets will generate a Hall current flowing in the perpendicular direction, thus providing an output.

Figure 8-1. Schematic description of experiment setup used to measure laser induced reflectance of a semiconductor sample. The transmittance can be measured by moving the detector.
Figure 8-2 Laser fluence calibration curve.

Figure 8-3. Photoelectromagnetic (PEM) detector.
FIG. (8-4) shows the synchronization between the Nd:YAG laser, the CO₂ laser and the data acquisition system. There are two synchronization signals available from the Nd:YAG laser, pre-pulse signal from the power supply and the internal photodiode located within the laser head. The delay between the pre-pulse signal and the actual optical pulse is adjustable. The pre-pulse signal then triggers the pulse generator which turns on and off the CO₂ laser. The pre-pulse is set to precede the optical pulse by 150 μs which allows enough time for a CO₂ laser pulse to stabilize before a Nd:YAG laser pulse arrives. The pulse width of the CO₂ laser can be varied from 20 μs to C.W. by adjusting the width TTL pulse width of the pulse generator. The detector output is displayed on the oscilloscope after ~ 200 ns delay. The delay was necessary because of strong high frequency noise picked up by the oscilloscope when the laser fires. The oscilloscope was triggered by the photodiode installed in the laser and pulse-averaged wave forms are recorded to be analyzed. According to the laser manual, the timing jitter between the photodiode and the laser pulse is less than 50 ps.
Figure 8-4. Data acquisition setup (above) and synchronization between the Nd:YAG and the CO₂ laser
Chapter 9
Results and Discussion

9.1 Si

FIG. (9-1) and FIG. (9-2) shows the time resolved transmittance of Si irradiated with 150 ps Nd:YAG laser pulses at 532 nm and 1064 nm wavelengths as the fluence increases. The transmittances shown are normalized with an intrinsic transmittance obtained without the Nd:YAG laser pulse. The decrease in the transmittance is clearly observed after Si is irradiated with a Nd:YAG laser pulse. FIG. (9-3) shows minimum transmittance achieved immediately after the laser irradiation. Note that the larger amount of laser fluence was necessary at 532 nm wavelength to achieve the same transmittance reduction obtained at 1064 nm wavelength. Possibly this can be explained by the fact that there are twice as many photons at 1064 nm as at 532 nm for a given fluence. As a result, provided that the two-photon and free carrier absorptions are negligible, the total number of carriers generated in the bulk is greater at the longer wavelength.

As the reduced transmittance recovers to its intrinsic value, there is a considerable difference in the time constants when Si is irradiated at 532 nm and 1064 nm wavelengths. Si has a considerably smaller interband absorption coefficient at 1064 nm wavelength (84.6 cm$^{-1}$ at 300 K) than at 532 nm wavelength ($1.0 \times 10^4$ cm$^{-1}$ at 300 K) because the optical absorption edge is very close to 1064 nm wavelength ($E_g = 1.155$ eV and $\hbar \omega = 1.165$ eV). The smaller absorption coefficient causes carriers to be distributed
in the larger volume resulting in less carrier density. According to Section 7-1, there are three types of carrier recombination, Auger ($\propto N^3$), radiative ($\propto N^3$) and SRH ($\propto N$) recombination. When Si is irradiated at 532 nm wavelength, the high carrier density causes fast Auger recombination to initially dominate. On the other hand, when Si is irradiated at 1064 nm wavelength, the carrier density is not enough for Auger recombination to dominate. Instead, the recombination is dominated by a much slower SRH recombination. The radiative recombination does not have a significant impact in Si because Si is an indirect-gap semiconductor. FIG. (9-4) shows integrated carrier density $\int_N(z,t)dz$ calculated according to Chapter 7 with constants provided in Table (9-1). As it was mentioned in Chapter 7, the SRH recombination rate and the surface recombination velocity depend on purity, dopant concentration and surface condition. In the calculation, the SRH recombination rate of $10^5$ s$^{-1}$ and the surface recombination velocity of $10^5$ cm s$^{-1}$ were used. These values are reasonable for a typical IR window grade Si with polished surface.$^{35}$
<table>
<thead>
<tr>
<th>Property</th>
<th>532 nm</th>
<th>1064 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambipolar diffusivity $D$ (cm$^2$ s$^{-1}$)$^a$</td>
<td>$18(300/T)$</td>
<td></td>
</tr>
<tr>
<td>Band gap $E_g$ (eV)$^b$</td>
<td>$1.16 - 7.02 \times 10^4 T^2/(T + 1108) - 1.5 \times 10^6 N^{1/3}$</td>
<td></td>
</tr>
<tr>
<td>Reflectance $\Gamma$</td>
<td>$0.37 + 5 \times 10^5 (T - 300)$</td>
<td>$0.30 + 5 \times 10^5 (T - 300)$</td>
</tr>
<tr>
<td>Reflectance $\Gamma$</td>
<td>$5.02 \times 10^4 (T/430)$</td>
<td></td>
</tr>
<tr>
<td>Reflectance $\Gamma$</td>
<td>$87.9 - 0.467T + 1.52 \times 10^3 T^2$</td>
<td></td>
</tr>
<tr>
<td>Reflectance $\Gamma$</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Reflectance $\Gamma$</td>
<td>Negligible</td>
<td></td>
</tr>
<tr>
<td>Interband absorption $\alpha$ (cm$^{-1}$)</td>
<td>532 nm</td>
<td>$5.02 \times 10^4 (T/430)$</td>
</tr>
<tr>
<td>Interband absorption $\alpha$ (cm$^{-1}$)</td>
<td>1064 nm</td>
<td></td>
</tr>
<tr>
<td>Interband absorption $\alpha$ (cm$^{-1}$)</td>
<td>532 nm</td>
<td>$87.9 - 0.467T + 1.52 \times 10^3 T^2$</td>
</tr>
<tr>
<td>Interband absorption $\alpha$ (cm$^{-1}$)</td>
<td>1064 nm</td>
<td></td>
</tr>
<tr>
<td>Two-photon absorption $\beta$ (cm/GW)</td>
<td>532 nm</td>
<td>Negligible</td>
</tr>
<tr>
<td>Two-photon absorption $\beta$ (cm/GW)</td>
<td>1064 nm</td>
<td></td>
</tr>
<tr>
<td>Two-photon absorption $\beta$ (cm/GW)</td>
<td>Negligible</td>
<td></td>
</tr>
<tr>
<td>Free-carrier absorption $\Theta$ (cm$^3$)</td>
<td>532 nm</td>
<td>$5 \times 10^{15} (T/300)$</td>
</tr>
<tr>
<td>Free-carrier absorption $\Theta$ (cm$^3$)</td>
<td>1064 nm</td>
<td></td>
</tr>
<tr>
<td>Free-carrier absorption $\Theta$ (cm$^3$)</td>
<td>Negligible</td>
<td></td>
</tr>
<tr>
<td>Auger recombination $r_1$ (cm$^6$ s$^{-1}$)$^b$</td>
<td>$3.8 \times 10^{-31}$</td>
<td></td>
</tr>
<tr>
<td>Auger recombination $r_1$ (cm$^6$ s$^{-1}$)$^b$</td>
<td>$5 \times 10^{-14}$</td>
<td></td>
</tr>
<tr>
<td>Radiative recombination $r_2$ (cm$^3$ s$^{-1}$)$^b$</td>
<td>$10^3 - 10^6$</td>
<td></td>
</tr>
<tr>
<td>SRH recombination $r_1$ (s$^{-1}$)$^b$</td>
<td>0.683</td>
<td></td>
</tr>
<tr>
<td>Lattice thermal diffusivity $D_L$ (cm$^2$ s$^{-1}$)$^b$</td>
<td>$1.978 + 3.54 \times 10^2 T - 3.68 T^2$</td>
<td></td>
</tr>
<tr>
<td>Lattice thermal diffusivity $D_L$ (cm$^2$ s$^{-1}$)$^b$</td>
<td>1585$T^{-1.23}$</td>
<td></td>
</tr>
<tr>
<td>Lattice thermal conductivity $\kappa_L$ (W cm$^{-1}$ K$^{-1}$)$^b$</td>
<td>$10^2 - 10^6$</td>
<td></td>
</tr>
</tbody>
</table>

a. REF. (47), b. REF. (35)

Figure 9-1. Time-resolved transmittance of Si irradiated at 532 nm wavelength
Figure 9-2. Time-resolved transmittance of Si irradiated at 1064 nm wavelength. Notice the considerably longer recovery time compared with the case of 532 nm.

Figure 9-3. Minimum transmittance of Si irradiated at 1064 nm and 532 nm wavelength.
Figure 9-4. Calculated laser-induced carrier density \( N(z, t) \) of Si integrated along z-axis

FIG. (9-5) and FIG. (9-6) shows detector outputs of CO\(_2\) laser pulses reflected from Si surface irradiated at 532 nm wavelength and its peak values at different laser fluence. The reflected pulses were too short to be resolved with this experimental setup. The pulse shapes seen in FIG (9-5) are nearly identical to the detector response function and the actual reflected pulse width is expected to be smaller than shown in FIG (9-5) (~2 ns). Also without precisely knowing the temporal structure of reflected pulses, absolute laser-induced reflectances could not be obtained.

When Si was irradiated at 1064 nm wavelength, the reflectance did not show any observable changes, which indicates that the surface carrier density was not high enough to induce changes in reflectance. FIG. (9-7) shows calculated surface carrier densities of Si irradiated at 1064 nm and 532 nm wavelengths. Since the surface condition (surface
recombination velocity) plays a significant role in the surface carrier density, surface recombination velocity of $10^2$ cm s$^{-1}$ and $10^5$ cm s$^{-1}$ were included to show the dependency. During the experiment, no increase in reflectance was observed when Si is irradiated at 1064 nm wavelength with a fluence of 60 mJ cm$^{-2}$. However, fluences as small as 5 mJ cm$^{-2}$ were sufficient to observe an increase in reflectance when Si is irradiated at 532 nm wavelength. Thus, from this observation and the calculated surface carrier density given in FIG. (9-7), it can be noted that the threshold carrier density to increase the reflectance must be at least $\sim 2 \times 10^{19}$ cm$^{-3}$.

Figure 9-5. Detector output of reflected CO$_2$ laser off Si surface irradiated with 532 nm Nd:YAG laser.
Figure 9-6. Peak reflectance of Si irradiated at 532 nm wavelength.

Figure 9-7. Calculated surface carrier density of Si irradiated at 1064 nm and 532 nm wavelengths with surface recombination velocity (SRV) $10^2$ and $10^5$ cm s$^{-1}$.
9.2 Ge

FIG. (9-8) and FIG. (9-9) shows time resolved transmittance of Ge irradiated at 532 nm and 1064 nm wavelengths. In contrast to Si, Ge did not show a significant difference in the time constant as the reduced transmittances recovers. This is because the band gap energy of Ge is 0.66 eV which is well below the photon energy of 1064 nm wavelength and the absorption coefficients at both wavelengths are quite high (1.4×10^4 at 1064 nm and 5×10^5 at 532 nm). FIG. (9-10) shows minimum transmittance of Ge immediately after the laser irradiation. As in the case of Si, higher fluence was necessary at 532 nm to achieve the same transmittance reduction obtained at 1064 nm.

![Graph showing time-resolved transmittance](image)

**Figure 9-8.** Time-resolved transmittance (normalized to the intrinsic value) of Ge irradiated at 532 nm wavelength.
Figure 9-9. Time-resolved transmittance of Ge irradiated at 1064 nm wavelength.

Figure 9-10. Minimum transmittance of Ge irradiated at 532 nm and 1064 nm wavelength.
FIG. (9-11) and FIG. (9-12) shows detector outputs of reflected CO$_2$ laser pulses from Ge surface irradiated at 532 nm and 1064 nm wavelength. Due to large absorption coefficients at both wavelengths, increased reflectance is observed when Ge is irradiated at both wavelengths. As in the case of Si, the temporal profiles seen in FIG. (9-11) and FIG. (9-12) correspond to the detector’s response and the actual temporal profile of reflected pulses could not be determined. FIG. (9-13) shows peak detector outputs of reflected pulses. While it appears that larger increase in reflectance is achieved when Ge is irradiated at 1064 nm, it cannot be so concluded without exactly knowing the reflected pulse widths.

![Figure 9-11. Detector output of reflected CO$_2$ laser pulses from Ge surface irradiated at 1064 nm wavelength.](image-url)
Figure 9-12. Detector output of reflected CO$_2$ laser pulses from Ge surface irradiated at 532 nm wavelength.

Figure 9-13. Peak detector output of CO$_2$ laser pulses reflected off Ge surface irradiated with 1064 nm and 532 nm Nd:YAG laser.
9.3 GaAs and CdTe

While Si and Ge are indirect-gap semiconductors, GaAs and CdTe are direct-gap semiconductors. As it was mentioned in Ch. 7, one characteristic of a direct-gap semiconductor is that it has high radiative recombination rate since the transition across the band gap does not require a phonon to conserve the momentum. In addition, GaAs and CdTe have similar band gaps (1.424 eV for GaAs and 1.475 eV for CdTe at room temperature) which are well above the energy at 1064 nm wavelength.

FIG. (9-14) and FIG. (9-15) show time resolved transmittance of GaAs irradiated at 532 nm and 1064 nm wavelengths and FIG. (9-16) shows minimum transmittances achieved as the laser fluence is increased. When GaAs is irradiated at 532 nm wavelength, its transmittance exhibited the fastest recovery time among all samples studied. The responses shown in FIG. (9-13) are near identical to that of the detector response function which indicates that the actual recovery time is less than 2 ns.

Despite photon energy being well below the band gap energy, reductions in the transmittance were observed when GaAs is irradiated at 1064 nm (1.165 eV) wavelength which is shown in FIG. (9-14). This indicates that sufficient carriers are still being generated as results of two-photon absorption and excitation through impurity levels.

FIG. (9-17) and FIG (9-18) show time resolved transmittance of CdTe irradiated at 532 nm and 1064 nm wavelengths and FIG. (9-19) shows minimum transmittances achieved as the laser fluence is increased. Similar to the case of GaAs, CdTe also showed significant reduction in transmittance when irradiated at 1064 nm despite photon energy being lower than the band gap energy.
FIG. (9-20) and FIG. (9-21) shows detector output of reflected CO$_2$ laser pulses from GaAs and CdTe surfaces irradiated with 532 nm Nd:YAG laser. Again the pulse shape shown corresponds to that of the detector response function. Thus, the actual reflected pulse width is expected to be less than 2 ns. FIG. (9-22) shows peak detector output as the laser fluence is increased. The peak reflectance initially increases linearly with the fluence followed by slight decrease. The decrease is due to the Nd:YAG laser-induced damage on the surface which became clearly visible as the fluence increased.

Figure 9-14. Time-resolved transmittance (normalized to the intrinsic value) of GaAs irradiated at 532 nm wavelength.
Figure 9-15. Time-resolved transmittance (normalized to the intrinsic value) of GaAs irradiated at 1064 nm wavelength.

Figure 9-16. Minimum transmittance of GaAs irradiated at 532 nm and 1064 nm wavelength.
Figure 9-17. Time-resolved transmittance (normalized to the intrinsic value) of CdTe irradiated at 532 nm wavelength.

Figure 9-18. Time-resolved transmittance (normalized to the intrinsic value) of CdTe irradiated at 1064 nm wavelength.
Figure 9-19. Minimum transmittance of CdTe irradiated at 532 nm and 1064 nm wavelength.

Figure 9-20. Detector output of reflected CO$_2$ laser pulses from GaAs surface irradiated at 532 nm wavelength.
Figure 9-21. Detector output of reflected CO$_2$ laser pulses from CdTe surface irradiated at 532 nm wavelength.

Figure 9-22. Peak detector output of CO$_2$ laser pulses reflected off GaAs and CdTe surfaces irradiated with 532 nm Nd:YAG laser.
9.4 Damage threshold

When measuring the Nd:YAG laser-induced transmittances and reflectances of a particular sample, the incident laser fluence was increased in steps until visible damage was clearly observed on the surface. Table (9-2) lists the fluences at which the damages were observed. It should be noted that "not so visible" damage and degradation of surface condition may occur well below these values.

Table 9-2. Nd:YAG laser fluence at which visible damage was observed on the surface. Omissions of a value indicate that no damage was observed at the maximum fluence (28.5 mJ cm\(^{-2}\) at 532 nm and 57.6 mJ cm\(^{-2}\) at 1064 nm).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wavelength nm</th>
<th>Fluence (150 ps pulse) mJ cm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>532</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1064</td>
<td>-</td>
</tr>
<tr>
<td>Ge</td>
<td>532</td>
<td>16.8</td>
</tr>
<tr>
<td></td>
<td>1064</td>
<td>33.1</td>
</tr>
<tr>
<td>GaAs</td>
<td>532</td>
<td>16.8</td>
</tr>
<tr>
<td></td>
<td>1064</td>
<td>-</td>
</tr>
<tr>
<td>CdTe</td>
<td>532</td>
<td>13.0</td>
</tr>
<tr>
<td></td>
<td>1064</td>
<td>-</td>
</tr>
</tbody>
</table>
Chapter 10
Conclusion

In part I, previously unreported THz spectrum and CO₂ laser (10.6 μm) induced IR emission spectrum of CH₃NO₂ were successfully obtained and reported. During the analysis of the THz spectrum, the model which was previously successful in analyzing the rotational-torsional transitions in the microwave region failed to correctly predict the peak of the convoluted THz spectrum. This suggests that there is still much to be learned in both experiment and theory. It is unfortunate that UH THz FEL is yet to be operational since the use of such equipment will no doubt drastically boost the experimental capacity in the THz frequency range.

There are a few things which should be considered in future work which will improve both the experimentally obtained and the calculated spectrum of CH₃NO₂. The maximum spectral resolution achievable with the IFS 66 v/S spectrometer is 0.25 cm⁻¹. In our experiment, the absorption spectrum was obtained by scanning over 16 hours for the background and sample spectra with the resolution of 1 cm⁻¹. Since the signal to noise ratio is proportional to a square root of scanning time and proportional to a spectral resolution, it was not practical to use any higher spectral resolution (smaller width) with current configuration of the FTIR. However, the resolution can be improved to 0.25 cm⁻¹ by using a Bolometer which can improve the signal to noise ratio by at least factor of 10. The Bolometer was not used in this work due to the high cost of liquid He, however, the use of it should be planned in the future work.
The calculation of rotational-torsional transitions of CH$_3$NO$_2$ can be improved by adding higher order term ($\sim J^6$) in the Watson's A-reduced Hamiltonian. In addition, rotational transitions within the second lowest vibrational mode (the lowest is the torsional mode) should be considered in the future work. According the Boltzmann distribution, approximately 8% of CH$_3$NO$_2$ will be in the first excited state of the second vibrational mode at room temperature. While transition frequencies between vibrational levels are much higher than the THz frequency range, rotational transitions within the same vibrational state will fall in the THz frequency range. Thus, even though the contribution from rotational transitions within the second vibrational mode in the THz frequency range may be small, it should be evaluated.

When CH$_3$NO$_2$ was vaporized and irradiated with a low power (19 W/cm$^2$) CO$_2$ laser, induced emission bands were observed both above and below the CO$_2$ laser frequency (943 cm$^{-1}$). While relative intensities of each emission band could not be determined due to an unknown loss factor of the FTIR, the spectral shapes clearly resembled those of absorption bands indicating that the observed spectrum is thermal emission from a laser-heated state. Even CH$_3$NO$_2$ was placed in the ambient atmospheric condition, we were still able to observe the emission and the presence of a buffer gas (air) did not alter shape of the emission bands.

It will be helpful to determine a statistical temperature of the laser-irradiated state of CH$_3$NO$_2$ to better quantify our result. This can be accomplished by simply using a calibrated blackbody source as a reference and should be considered when continuing this work. Also, to better understand the emission mechanism, it will be interesting to know
how the emission spectrum, the intensity and the lifetime depend on a laser frequency, laser intensity, pressure, and a type of buffer gas.

Optical properties of optically excited polycrystalline Si, Ge, GaAs, and CdTe were studied by exciting the materials with 150 ps 532 nm and 1064 nm wavelength laser pulses and measuring the time-resolved reflectance and transmittance of 10.6 μm wavelength CO₂ laser beam incident on the surface oriented at the Brewster angle. When the samples were irradiated at well above the band gap energies, they all exhibited sub-nanosecond increase in reflectance. However, when these samples were irradiated at very near or below the band gap energy, the carrier densities did not reach high enough value to increase reflectance due to low absorption coefficients. The threshold carrier density for Si to induce added-reflectance at 10.6 μm was determined to be greater than 2 × 10¹⁹ cm⁻³ according to the experimental results and calculations. Due to the limited time resolution of the electronics (i.e. detector, pre-amplifier and oscilloscope), the absolute induced reflectance and the reflected pulse width could not be determined. Short reflected pulses imply that the Auger and/or radiative recombination processes, which dominate at high carrier density, quickly decrease the carrier density below the threshold required to increase the reflectance at 10.6 μm. However, according to the Drude model, this threshold will be lowered as the frequency decreases (e.g. in the THz frequency range). Thus, it is possible for the threshold carrier density to be below where Auger and radiative recombinations are the dominant processes of recombination. In such a case, it is expected that duration of the laser-induced reflectance will be longer in the THz frequency range. In fact, several authors have demonstrated laser-induced
reflectance lasting over 50 ns at selected THz frequencies using various high resistivity single crystal semiconductors\textsuperscript{33-34}.

In addition to the increased reflectance, reduction in transmittance was observed when samples were irradiated with 150 ps pulse width at 532 nm and 1064 nm wavelengths. As the reduced transmittance recovers to its intrinsic value, the time constant varied from less than 2 ns (GaAs irradiated at 532 nm wavelength) to greater than 100 $\mu$s (Si irradiated at 1064 nm wavelength) depending on a sample and the incident laser wavelength. Even when the samples were irradiated at below the band gap energy (GaAs and CdTe irradiated at 1064 nm wavelength), enough carriers were generated via two-photon absorption and excitations through impurity levels for a CO$_2$ laser pulse to be absorbed. Similar to the reflectance, the decreased transmittance is expected to last longer in the THz frequency range according to the Drude model. This may be undesirable in some cases since the prolonged increase in absorption will mean a longer dead time of a laser-activated semiconductor switch.

To better understand the carrier dynamics and induced changes in optical properties, the absolute values and temporal structure of laser-induced reflected pulses are clearly necessary. One way to accomplish this may be to evaluate the reflected pulse in the frequency domain using an Etalon, or even an FTIR. With enough spectral resolution and a sensitive detector, this may be possible and should be carefully evaluated in the future. Also using laser-induced absorption, it is possible to gate the Ge filter which was placed in front of the detector. While the time resolution achieved in this way is limited by the pulse width of the Nd:YAG laser (150 ps), it is far better than the $\sim$2 ns resolution achieved in this experiment.

102
In this experiment, subnanosecond CO₂ laser pulses were generated by irradiating polycrystalline semiconductors oriented at the Brewster angle with 150 ps 532 nm and 1064 nm wavelength laser pulses. The next step of this project is to study the laser-induced reflectance and transmittance in the THz frequency range. This can be accomplished if the UH THz FEL becomes operational or when the Bruker IFS 66v/S Fourier transform spectrometer is upgraded to perform step scans, the ability to perform time-resolved (5 ns resolution) Fourier transform spectroscopy. Since the duration of induced reflectance is expected to last longer, 5 ns resolution may be sufficient at THz frequencies.

From the results of this experiment, it appears that, polycrystalline Si is best suited for the cavity dump application among the materials studied because of its high damage threshold subject to the Nd:YAG laser. As shown in Chapter 9, even though all the materials studied showed increase in reflectance when irradiated with the Nd:YAG laser, they have relatively low damage threshold except Si.

To see if the Drude model can predict the induced reflectance and transmittance correctly, carrier density, reflectance and transmittance for Si were calculated according to Chapter 7. However, calculated reflectance and transmittance did not fit the experimental result simultaneously by adjusting effective mass and carrier relaxation time appearing in EQ. (7-14). One possible reason why the Drude model did not work at the wavelength of the probe beam 10.6 μm is that the period of 10.6 μm wavelength is comparable to a typical carrier relaxation time τ (10⁻¹⁴ ~ 10⁻¹⁵)⁴⁷. The Drude model is known to work relatively well in frequencies either well above the plasma frequency or
well below the relaxation frequency \( (1/\tau) \). Thus, the Drude model may not be a suitable model to predict dielectric constants at 10.6 \( \mu \text{m} \) wavelength.

It will be interesting to see if there is a clear advantage in using a polycrystalline material rather than a single crystal material. The side by side comparison of laser-induced changes in optical properties should be made in the future.
Appendix

In addition to the THz spectroscopy and the CO₂ laser-induced spectroscopy of CH₃NO₂, absorption spectra of other solid explosives {Pentolite [mixture of trinitrotoluene (TNT) and pentaerythritol tetranitrate (PETN)], cyclotrimethylene-trinitramine (RDX), cyclotetramethylene-tetranitramine (HMX)} in the THz and the mid-infrared frequency range were acquired with the IFS 66v/S spectrometer. RDX and HMX were provided by Ordnance Systems Inc., and pentolite was provided by Accurate Energetic Systems, LLC. While spectral features of these materials in wide range of frequencies are found in numerous papers¹-⁷, our results should serve as cross reference purposes.

FIG. (A-1) through FIG (A-3) show absorption spectra of three explosives mentioned above in a powdered form. All materials came as a powdered form and these materials were simply deposited on a polyethylene film by sprinkling over it. The absorption spectra shown on the top of figures are obtained by simply taking a logarithm of transmittance \[\alpha = -\ln(T)\]. The initial increase in the absorption is due to an increasing scattering loss as the wavelength becomes comparable to a size of the particles. To show the locations of absorption peaks more clearly, a background of each spectrum was obtained by fitting a polynomial (9th order) and the background is subtracted from the spectrum as shown in the bottom parts of figures.
Figure A-1. Absorption spectrum of pentolite (top-black). The background (top-red) is subtracted to show the locations of absorption peak more clearly (bottom).

Figure A-2. Absorption spectrum of HMX (top-black). The background (top-red) is subtracted to show the locations of absorption peak more clearly (bottom).
Figure A-3. Absorption spectrum of HMX (top-black). The background (top-red) is subtracted to show the locations of absorption peak more clearly (bottom).
References


