Terahertz absorption spectra of highly energetic chemicals

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ABSTRACT

Research into absorption spectra is useful for detecting chemicals in the field. Each molecule absorbs a set of specific frequencies, which are dependent on the molecule's structure. While theoretical models are available for predicting the absorption frequencies of a particular molecule, experimental measurements are a more reliable method of determining a molecule's actual absorption behavior. The goal of this research is to explore chemical markers (absorption frequencies) that can be used to identify highly energetic molecules of interest to the remote sensing community. Particular attention was paid to the frequency ranges located within the terahertz transmission windows of the atmosphere. In addition, theoretical derivations, with the purpose of calculating the detection limits of such chemicals, will also be presented.

Keywords: Terahertz, Spectroscopy

1. INTRODUCTION

Researchers have been investigating the detection of solid and liquid forms of highly energetic chemicals in recent years¹⁻⁵. Wilkinson et al. measured the absorption spectrum of solid triacetone triperoxide (TATP) in the terahertz region for the first time this past year¹. This project was initiated to determine the practicality of detecting vapor-phase highly energetic chemicals in the terahertz (THz) region. A series of absorption measurements have been performed under controlled conditions, allowing detection limits to be established. The detection limits will vary with stand-off distance to the sample and gaseous sample concentration. Both highly energetic chemicals and their constituents were investigated between 20 and 80 wavenumbers (cm⁻¹), 0.6 THz to 2.4 THz, with particular attention to atmospheric transmission windows in the THz region, as these frequencies would be the most useful for remote sensing under field conditions.

2. EXPERIMENT

2.1 Set-up

The data was collected using a Bruker IFS 66v Fourier transform (FTIR) spectrometer with a variable pathlength gas cell from Pike Technologies mounted in the sample compartment. A cryogenically cooled IR Labs silicon bolometer was used as the detector. Figure 1 shows the experimental set-up.

Several highly energetic chemicals were identified for investigation in this experiment. Those samples that could not be obtained through standard channel suppliers, such as Fisher Scientific, were synthesized in the laboratory. All synthesized chemicals were verified and characterized via standard IR and mid-IR chemical spectroscopy measurements and verified against known IR spectra. The samples are kept in glass sample tubes which are evacuated to remove any air. The sample then sublimates or evaporates inside the glass sample tube until reaching equilibrium pressure.

The optics and source for the FTIR spectrometer used in the measurements required optimization to operate in the long wavelength region. The FTIR was equipped with a 125 Watt mercury arc lamp and 23μ m thick mylar beam splitter, providing good spectral range from 20 cm⁻¹ to 80 cm⁻¹. The variable pathlength gas cell has

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(a) Bruker IFS 66v with variable pathlength absorption cell (center) and cryogenically cooled silcon bolometer (left).

(b) Block diagram of experiment

Figure 1: Experimental Set-up

z-cut quartz windows allowing radiation below 200 cm⁻¹ to pass through with little attenuation. The blackbody source radiation entering the absorption cell follows an adjustable folded-path scheme through the cell allowing for pathlengths ranging from 1 to 7 meters. The gas cell protrudes from the sample chamber leaving portions of the beam path open to ambient atmosphere, so an air-tight lid was designed to seal the cell region exposed to atmosphere. Dry N_2 gas was used to purge the sealed volume in order to remove any remaining water vapor that might affect the measurements. The gas cell has two ports for access into the cell. One port is connected to an external vacuum pump, the other port is connected to the sample apparatus. Sample gas is introduced into the cell through one of the ports and the pressure is measured using dual MKS pressure sensors. The sample can then be diluted with air in a controlled way. Measurements are taken under different concentrations, pathlength, pressures and dilution ratios.

2.2 Theory

Transmission data, such as that shown in Figure 2, is collected using the FTIR and the variable pathlength absorption cell. The sample gas is released into the absorption cell and transmission through the sample is collected at 1 meter intervals from 2 to 6 meters in pathlength. This transmission corresponds to:

$$T = I_o \exp^{-\alpha * L} \tag{1}$$

where T = the normalized transmission from the FTIR, $I_o \equiv 1$, $\alpha =$ absorption coefficient and L = pathlength. Solving for αL ,

$$-\ln T = \alpha L \tag{2}$$

Equation (2) can also be rewritten as:

$$-\ln T_n = \alpha L_n \tag{3}$$

where *n* denotes the different pathlengths. Graphing $-\ln(T)$ vs. *L* gives α as the slope of a linear least squares fit, as seen in Figure 3. After calculating α at each data point, the absorption coefficients are then graphed as a function of wavenumber. Variation of the absorption coefficient with frequency is shown in Figure 4. The technique described before is repeated for each chemical sample.



Figure 2: Example of transmission data through 1.6 Torr of Nitromethane taken from 2 to 6 meters.



Figure 3: At each nitromethane data point collected $-\ln T$ vs. L is graphed and a least squares fit of the absorption coefficient is calculated. Here, the data collected at 20.1284 cm⁻¹ is examined.



Figure 4: Nitromethane absorption coefficients calculated using the linear least squares fit at each data point. The absorption coefficient, in black, is graphed as a function of wavenumber. Error bars are in grey.

3. RESULTS

3.1 Atmosphere

Initial measurements were made using air at various humidities. Water is an extremely absorbent molecule in the terahertz region and its presence in the atmosphere poses a challenge for remote sensing. For this reason, air from the surrounding laboratory was released into the absorption cell to determine the location of the transmission windows in the atmosphere. Transmission "windows" are areas of low absorption in air. Spectra collected in these window regions allow measurements to be collected with minimal secondary water absorption. Figure 5 shows the absorption spectra of air taken from the laboratory with a relative humidity of 46%. It is useful to note that atmospheric absorption increases significantly above 32 cm^{-1} .



Figure 5: Example of transmission data through 750 Torr air, 46% relative humidity, at a pathlength of 6 meters.

3.2 TATP and Acetone

Acetone (CAS 67-64-1) is a component of triacetone triperoxide (TATP) (CAS 17088-37-8), both in its production and decomposition. Acetone has a vapor pressure of 186 Torr at 20 °C and a dipole moment of $2.91D^{6,7}$ and therefore has strong absorption spectra. The acetone used for this measurement was obtained from Fisher Scientific with a purity of 99.5%.



Figure 6: Absorption spectra of Acetone measured at path lengths ranging from 2 to 6 meters. The absorption spectra shows that Acetone exhibits strong absorption below 50 cm^{-1} .

TATP crystals were placed in a glass sample tube. The air was evacuated, allowing the TATP to sublimate in the tube. The resultant gas was admitted into the absorption cell and measured. Figure 7 shows that TATP and its reagents has measurable spectra between 20 and 50 wavenumbers (cm^{-1}).



Figure 7: Absorption spectra of TATP and its reagents measured at pathlengths ranging from 2 to 6 meters. The absorption spectra shows that TATP has absorption lines below 52 cm^{-1} .

Samples of poor quality synthesis of TATP were obtained for comparison. Figure 8 shows the absorption spectra at a pathlength of 6 meters. While the sample does not exhibit the same strongly absorping spectra as TATP, it does show absorption below 40 cm^{-1} .s



Figure 8: A example of an poor quality synthesis of TATP was obtained and measured for comparison against higher quality TATP. The spectra was measured using a 6 meter pathlength cell and shows absorption below 40 cm^{-1} .

3.3 Nitromethane

Nitromethane (CAS 75-52-5) is one of the more simple nitro compounds, but serves as a prototype for other highly energetic chemicals such as TNT and RDX. Our nitromethane sample was obtained from Fisher Scientific with 99% purity. It shows strong absorption below 45 cm^{-1} , as seen in Figure 2, driven by a dipole moment of 3.46 Debye (D).

Using a constant pathlength of 6 meters, varying amounts of nitromethane were diluted with 1atm (approx. 757 Torr) of air from the surrounding laboratory. The relative humidity of the laboratory air was 28%. Figure 9 shows the absorption spectra of the diluted nitromethane in addition to the spectra from the water present in

the atmosphere. The strong absorption lines due to water vapor are located at 25 cm^{-1} , 33 cm^{-1} , 37 cm^{-1} and 39 cm^{-1} . A 100% transmission line is shown in black for comparison. Note that even at the lowest concentration in air, 52.7 ppm, the nitromethane still showed measurable absorption.



Figure 9: The absorption spectra of nitromethane diluted with air from the surrounding laboratory was measured using a constant 6 meter pathlength. The amount of nitromethane present in the absorption cell was 40 mTorr, 100 mT, 230 mT, 401mT and 548mT respectively. Note the strong water absorption at 25 cm⁻¹, 33 cm⁻¹, 37 cm⁻¹ and 39 cm⁻¹.

4. DISCUSSION

4.1 Application to Field Detection

One simple geometry in detecting airborne chemicals in field situations is to view a blackbody and monitor changes in power over particular frequency regions. A description of blackbody power calculations follows. Blackbody theory has been discussed by many authors, so here we briefly summarize the results by Kingston⁸.



Figure 10: Diagram showing an object at temperature, T, with a lens a distance, R, away from the object.

Using Planck's law it can be shown that the total radiance of an object is

$$H_A = \int_{\nu_1}^{\nu_2} \varepsilon(\nu) \frac{2\pi h \upsilon^3}{c^2 (e^{\frac{h \upsilon}{kT}} - 1)} d\nu$$
(4)

where H = the spectral radiance of the object, $\varepsilon(\nu)$ is the emissivity of the object, h is Planck's constant, c the speed of light and k is Boltzman's constant. By integrating over a range of frequencies, the total radiance of the object within those frequencies can be calculated, with the resultant quantity in units of Watts/m².

The power from the blackbody object is equal to the intensity of the radiation crossing the hemisphere containing the object, as seen in equation (5). The intensity, I_s , varies with $\cos \theta$ such that $I_s = I_{s_o} \cos \theta$.

$$P_{total} = H_A A = \int_0^{2\pi} I_{s_o} \cos \theta R^2 d\Omega_s \tag{5}$$

From equation (7), it is possible to solve for I_{s_o} ,

$$I_{s_o} = \frac{H_A A}{\pi R^2} \tag{6}$$

and thus, I_s ,

$$I_s = \frac{H_A A \cos \theta}{\pi R^2} = H_A \frac{\Omega_A}{\pi}.$$
(7)

The power seen by a lens situated at hemisphere, S, is then,

$$P_s = I_s A_{lens} \tag{8}$$

where A_{lens} = the area of the lens.

4.2 Detection Limits



Figure 11: Example of situation with a cloud between the observer and a blackbody source, the wall.

It is useful to consider the limits on detecting various molecules. First we consider the SNR of the source/detector combination. A diode used as a coherent radiometer has an NEP of 3.77×10^{-20} Watts/Hz. A coherent radiometer viewing a 1 m² blackbody source at a distance of 100 m with a lens size of 0.5 m² would measure 3×10^{-9} Watts. For these calculations a bandwidth of 3 GHz was used as this corresponds to the average linewidth of a spectral line pressure broadened with 1 atm of air.

Therefore, when considering the detectability of these chemicals out in the field, the limiting factor would not be the signal to noise ratio (SNR) of the detector, rather, the limiting factor would likely be the atmospheric effects. Previously it was stated in equation (1) that

$$T = e^{-\alpha * L}$$

Preliminary measurements using air and the technique as described in Section 2.2 yielded an absorption coefficient of $\alpha = 0.005779$ (1/m) at a wavelength of 20.0078 cm⁻¹. Over a pathlength of 100 meters this corresponds to a 56% decrease in transmitted power due to atmospheric effects alone.

Using the equation

$$P = kTB \tag{9}$$

where k = Boltzman's constant, T = temperature (K) and B = bandwidth (Hz), it is possible to relate a small change in transmitted power to a change in perceived temperature. If one were to measure the power emitted from a blackbody source at 300K at a distance of 100 meters and α were to change by 0.00018 m⁻¹, or approximately 3%, the perceived temperature of the blackbody would change by 2%.

5. CONCLUSION

The absorption spectra of highly energetic, vapor-phase chemicals Nitromethane, Acetone and Triacetone Triperoxide were measured in order to determine the practicality of detecting them remotely. Particular attention was given to those absorption frequencies that coincide with atmospheric windows in the terahertz region to increase the likelihood of collecting only the highly energetic chemical spectra. Using a variable path absorption cell, the absorption spectra were measured at one meter intervals between 2 and 6 meters at a resolution of 0.2 cm^{-1} . From this data, detection limits were established as to the amount of chemical needed in the atmosphere in order to affect a large enough change in power for a reasonable detector to sense it.

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