

Terahertz Spectroscopy of TNT for Explosive Detection

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ABSTRACT

Transmittance spectra of solid and vapor samples of trinitrotoluene (TNT) in the spectral range 0.6 to 10 THz at resolutions up to 1 GHz are reported. Uniform solid samples of ~100 μm thickness gave stronger absorption and more resolved structure than previous studies. New absorption lines for TNT solid below 100 cm^{-1} are reported. A heated 10 m multipass White cell was used for spectroscopy of the vapor. Strong absorption bands yield unexpectedly large absorption cross sections for the anticipated saturated vapor pressure at the cell temperature, leaving their assignment to TNT in doubt. These results indicate that path lengths exceeding 10 m and temperatures higher than 40 C, or significantly higher instrumental sensitivity, are needed for sensing of TNT vapor in the spectral range 0.6 to 10 THz.

Keywords: TNT, explosives, terahertz, millimeter wave, infrared

1. INTRODUCTION

Spectral sensing of explosive material requires a-priori knowledge of characteristic absorption features. Terahertz spectra of both solid and vapor phase of TNT are necessary for devising sensing strategies for detection of explosives. There have been several recent publications that present the mid- and far-IR spectrum of solid TNT [1-3]. The low vapor pressure and concentration of TNT is a significant challenge for vapor phase spectroscopic detection. Recently, the vapor spectrum of the significantly more volatile DNT was reported in the range 0.05 to 2.7 THz ($2\text{-}90\text{ cm}^{-1}$) [4]. Mid-IR TNT vapor spectra for wavenumbers above 1000 cm^{-1} are known [5]. However, there appear to be no published THz or mm-wave spectroscopic measurements on vapors of whole TNT molecules [6].

In this work, we present the measured transmittance spectra of solid and vapor samples of TNT in the spectral range 0.6 to 150 THz at resolutions up to 1 GHz. New absorption lines for TNT solid below 100 cm^{-1} are reported. The vapor phase measurements presented here serve mainly to place lower bounds on necessary path length, temperature, and instrumental sensitivity.

2. EXPERIMENTAL DETAILS

The melting temperature of 2,4,6-trinitrotoluene (TNT) $\text{C}_7\text{H}_5\text{N}_3\text{O}_6$ is 81 C, which allows it to be liquefied easily. It is non-hygroscopic and can be easily dried. It does not react with metals. TNT is toxic, and can be absorbed through skin, causing irritation and yellow staining. Long-term contact and inhalation cause many serious health problems, so that gloves, eye protection, and ventilation are required for safe handling. The molecular weight of TNT is 227.15 g/mol, and the specific gravity is 1.654, so that the number density of molecules in the solid is $4.4 \times 10^{21}\text{ cm}^{-3}$.

A 1 g sample of TNT, mixed with 30% water for stability, was obtained from Chem Service Inc, [www.chemservice.com]. The sample had the appearance and consistency of sticky pale-yellow snow. This wet TNT was heated in a test tube in hot water maintained below 81 C for several hours. The sample evolved moisture, which condensed on the inner walls of the test tube. Heating was maintained until the condensation eventually evaporated and no more moisture was evolved. Subsequently, the water was brought to a boil, and the TNT melted to a clear yellow fluid, when it was poured from the test-tube onto various substrates. Chips of solid TNT could also be melted directly on substrates using a hot plate.

To prepare thin solid films for far-IR spectroscopy below 10 THz, TNT was melted on a polyethylene substrate on a temperature controlled hot plate. A weighted PTFE (Teflon®) flat was set atop the pool to spread the liquid into a uniform film approximately 0.1 mm thick. After the sample cooled, it separated easily from the Teflon plate, but it adhered to the polyethylene, which then served as a transparent substrate for THz spectroscopy.

A vacuum-bench BOMEM Model DA8 FTIR spectrometer collected transmittance spectra with apodized spectral resolution up to 0.04 cm^{-1} . To collect spectra in the range $20\text{-}95\text{ cm}^{-1}$, a 50 micron mylar pellicle beamsplitter and Hg-arc lamp blackbody source were used with a 4 K Si bolometer having a 100 cm^{-1} low pass filter. These spectra had a gap between $55\text{ and }70\text{ cm}^{-1}$ where the signal-to-noise ratio was poor due to poor modulation efficiency of the beamsplitter. A $25\text{ }\mu\text{m}$ mylar pellicle and 4 K silicon bolometer (Infrared Labs) were used for continuous coverage of the range $30\text{-}100\text{ cm}^{-1}$. A globar blackbody, $3\text{ }\mu\text{m}$ -thick mylar pellicle beamsplitter, and room temperature DTGS detector gave spectral coverage of $100\text{-}660\text{ cm}^{-1}$ for studies of the solid. Vapor spectra in the range $75\text{-}370\text{ cm}^{-1}$ were collected using the $3\text{ }\mu\text{m}$ beamsplitter, globar source, and 4 K bolometer with 370 cm^{-1} low pass filter.

The modulated beam from the interferometer passed through the evacuated sample compartment, where the TNT film on its substrate was placed at the beam focus with an adjustable iris to control the region probed. After the sample, beam was collected by an off axis ellipsoidal mirror and focused onto the detector. Reference spectra were collected using clean substrates.

Vapor phase spectra used a heated 10-meter fixed length multi-pass White cell (Fig. 1), which was contained entirely within the spectrometer vacuum compartment. This Pyrex cell had a volume of 2.3 liters, an overall length of 40 cm, and had permanently aligned ceramic-protected silver-coated mirrors epoxied to the inner walls. The optical through-put of the cell was matched to that of spectrometer when its adjustable source aperture was less than or equal to 5 mm diameter. The windows were 25 mm diameter polyethylene disks for measurements below 10 THz. The cell was tested for leaks with a helium leak detector and found to hold and both vacuum and over-pressure. The cell contained a pair of valved gas ports, to one of which was attached a metal cup containing a TNT sample, while the other was attached to a turbo-molecular pump station. The pressure of the cell was monitored with a thermocouple gauge in the vacuum line. The vacuum pump had its own valve so that it could be isolated from the cell. Uniform heating of all surfaces exposed to TNT vapor is required, since the concentration of vapor is determined by the temperature of the coldest exposed surface. A copper shroud was built to enclose the glass tube of the 10 m cell. Six 100 ohm 25 W power resistors were screwed via their heat sinks to the copper shroud. The pyrex walls of the cell were heated radiatively while the aluminum end plates that support the pyrex tube, windows, and ports were heated conductively. Up to 35 VAC was applied using a Variac to the power resistors in the vacuum sample compartment of the spectrometer. A heavy copper strap was connected between the copper shroud and metal cup that contained the solid TNT sample. This sample cup was screwed via pipe threads directly to one of the cell outlet valves. The entire system was then draped in fiberglass cloth. Heating of all surfaces of the 10 m cell was found by touch to be fairly uniform. A thermocouple temperature sensor was thermally anchored to the TNT cup. Since the sample cup was the farthest element of the system from the heating elements, its temperature should be lower than that of any other exposed surface within the cell. This was done intentionally to avoid thermal transport of solid TNT to mirrors or windows of the cell. The single remaining port on the cell was used for evacuation. The cell could be completely sealed off from the pump and sample cup by closing valves that are completely contained within the heating shroud. Vacuum feed-throughs in the spectrometer's sample-compartment walls permitted electrical access to the thermocouple and to the heater elements.

The procedure for collecting the vapor spectra in the range $20\text{-}370\text{ cm}^{-1}$ was as follows. The 10 m cell was heated to 40 C and evacuated continuously for several hours with the TNT sample cup open to the cell in order to eliminate as much as possible all volatile substances from the sample and the internal walls of the vapor cell system. Then the valve to the TNT sample cup was closed, while pumping on the cell continued. After several hours pumping on the heated cell, the valve at the cell to the pump-line was closed and multiple reference spectra were collected. Each reference spectrum was the co-addition of 100 scans of the spectrometer mirror. The total time to acquire one high resolution spectrum was ~1 hour. During this time the pressure in the cell would rise from ~70 mT to about 300 mT due to outgassing from the cell walls. After each reference spectrum was collected, the cell was evacuated again to a pressure of ~70 mT. Then the pump port was sealed again by closing the valve at the cell, and the next reference spectrum was collected. After all reference spectra were collected, the second cell valve was opened to expose the cell to vapors contained in the TNT

sample cup. Then multiple sample spectra were collected, with the same number of coadditions and same duration in each one. With TNT sample cup open to the cell, the pressure in the cell rose to ~ 500 mT during the course of the measurement. After all sample and reference spectra were collected, they were coadded and divided to produce a single transmittance spectrum. The total number of coadded scans was 250 in the $75\text{-}370\text{ cm}^{-1}$ range. For the $20\text{-}55\text{ cm}^{-1}$ range, it was 400.



Fig. 1. Multipass 10 m White cell. Input and output are via turning mirrors and vacuum windows on the right. Internal mirrors are evident on the left. The entire system was heated using a copper shroud.

The highest temperature that could be achieved with the 10 m cell was 50 C. Above this temperature, the spectrometer began to malfunction due to overheating of the electronics. Even at the operating temperature of 40 C, it was noted that plastic parts on the cell exterior began to decompose, leaving an oily deposit on interior spectrometer walls, and the epoxy that held the mirrors internal to the cell turned brown.

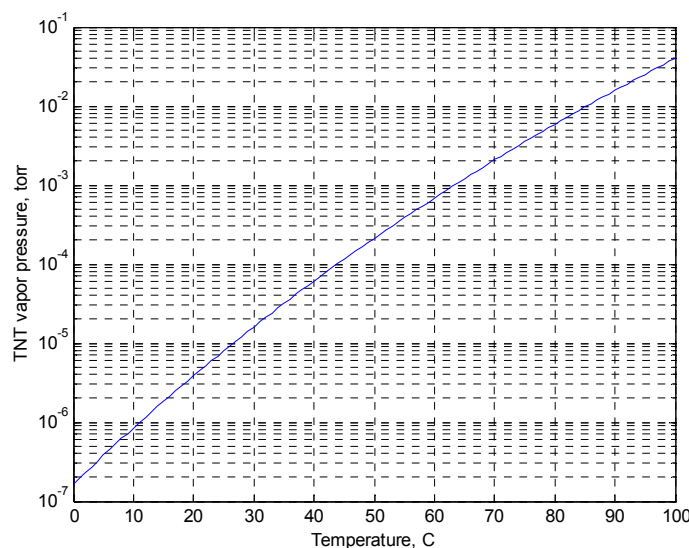


Fig. 2. TNT vapor pressure vs. temperature.

For an ideal gas, absorbance = $(P/kT) \sigma z$, where P is the variable pressure, k Boltzmann's constant, T the constant temperature, σ absorption cross section, and z the constant optical path length. The room temperature vapor pressure of

TNT is just below 10^{-5} Torr according to [7]. At such low pressures, the change in transmittance of a beam that passes through 10 m of vapor would be only 0.03% for an absorption cross section as large as 10^{-18} cm^2 . The expected difficulties in detecting such weak absorption with our system motivated the heating of the vapor cell. Fig. 2 presents the temperature dependence of the vapor pressure calculated with empirical coefficients for TNT in the Clausius-Clapeyron equation. When temperature is increased from 20 to 40 C, the vapor pressure increases 15 times. The change in transmittance due to an absorption line with 10^{-18} cm^2 cross section for 10 m path length would then increase to 0.5%, which might be detectable given sufficient signal-to-noise ratio.

3. RESULTS

3.1 Solid TNT

Fig. 3 presents the spectrum of solid TNT in the range 30-660 cm^{-1} at resolution 1 cm^{-1} . This same range has been reported in [1,2], but the lines in Fig. 3 are much stronger than those studies because our sample was thicker. We find in Fig. 3 all previously reported lines, namely those at 123, 157, 186, 272, 305, 325, 355, 453, 603, and 639 cm^{-1} . However, we are able to resolve more structure in our spectrum. For example, the strong 350 cm^{-1} line is here revealed to be a doublet. We find a previously unreported line at 525 cm^{-1} , and the lines revealed below 100 cm^{-1} in Fig. 3 (right) are apparently new.

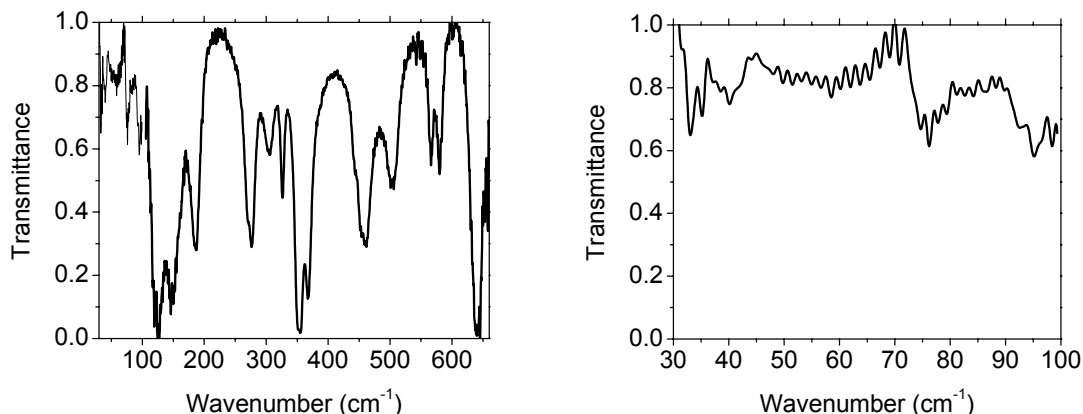


Fig. 3. (left) Far-IR spectrum of ~ 0.1 mm thick sample of solid TNT. (right) Detail of long wave portion showing weak absorption features. The fast oscillations are Fabry-Perot resonances in the polyethylene substrate, and the broad derivative-like structure near 70 cm^{-1} is likewise an artifact due to a polyethylene absorption band.

As an example calculation of the absorption cross section, we consider the line in Fig. 3 at ~ 275 cm^{-1} . The minimum transmittance is 0.3, giving an absorbance value of 1.2, and with a 0.1 mm sample thickness, the absorption coefficient is found to be 120 cm^{-1} . Using the concentration of molecules in the solid gives an absorption cross section of about 2.7×10^{-20} cm^2 . This value is reasonable for a molecular vibration [8]. Clearly TNT has vibrational modes with larger cross sections than this, although the deepest lines in our spectrum cannot be quantitatively analyzed.

3.2 TNT Vapor

Fig. 4 presents the transmittance spectrum of vapor in the range 70-370 cm^{-1} at 0.04 cm^{-1} resolution. In this experiment the cell and TNT sample were unheated at the laboratory temperature of about 23 C. Consequently, the walls of the cell retained a significant amount of adsorbed water, which outgassed into the cell during the measurement, giving prominent sharp water lines in Fig. 4. Beside these, three broad absorption features appear as indicated by arrows. Moreover, the baseline of the spectrum reveals an oscillatory structure, with varying period, most evident around the broad feature near 250 cm^{-1} . In addition to the broad bands in Fig. 4, some sharp lines appeared, which were absent in the reference, with widths similar to the water lines. These lines occurred at 81.0, 82.6, 124.6, 135.8, 144.9, and 152.5 cm^{-1} . The minimum transmittance of these lines relative to the baseline is of order 90%, which implies an absorbance of 0.1. The absorption coefficient α considering the 10 m path length is therefore 10^{-4} cm^{-1} . The vapor pressure of TNT is at most 10^{-5} Torr, which corresponds to a concentration 3.2×10^{11} cm^{-3} in the cell. Thus, the peak absorption cross section per molecule for these lines would have to be $\sim 10^{-16}$ cm^2 , a surprisingly large value when compared to the cross section for molecules in the solid. This casts doubt that any of the features in Fig. 4 are actually due to TNT. Indeed, the main value of Fig. 4

may be to emphasize the difficulty in observing any THz feature definitely attributable to TNT vapor at ambient temperature, even for path lengths as long as 10 m.

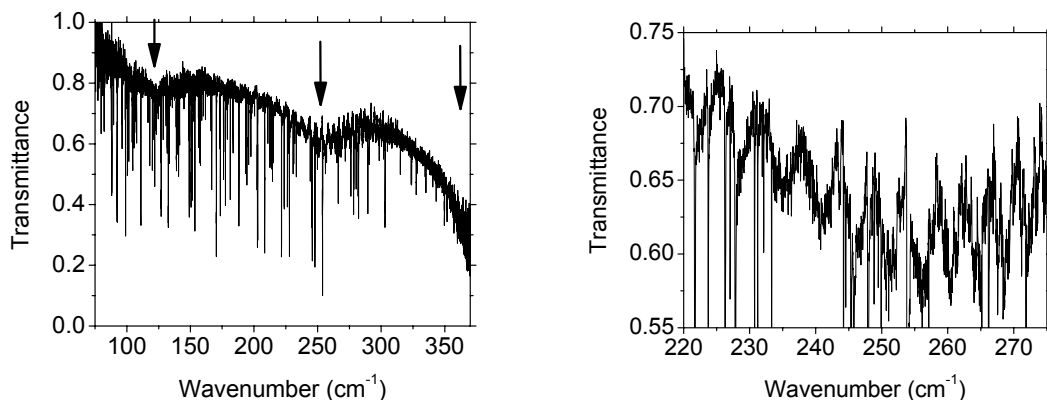


Fig. 4. (left) Transmittance spectrum of 10 m vapor cell containing TNT at ambient temperature. (right) Detail.

Figure 5 presents a TNT spectrum in the ranges 20-55 and 70-95 cm^{-1} , for which the 10 m cell was heated to ~ 40 C. Heating facilitated the removal of adsorbed water from the cell walls prior to the experiment, so that the resulting spectra are nearly free of water lines. In Fig. 5 (left), the most prominent feature is the strong decrease in transmittance below 35 cm^{-1} . Such a feature is characteristic of many molecular vapors, e.g. acetone and methanol [8], and results from unresolved absorption lines of pure rotational transitions. In the present case, for a minimum transmittance of about 20% and an estimated TNT vapor pressure at 40 C of $\sim 6 \times 10^{-5}$ Torr, we estimate a maximum cross section of 9×10^{-16} cm^2 . This is a surprisingly large value for molecular absorption. There is also some periodic structure on the baseline with a maximum depth of about 10%, which gives a maximum cross section of order 6×10^{-17} cm^2 , still a very large value. These giant cross section estimates suggest that all features may be assigned more reasonably to unidentified out-gassed vapors from the sample cell, or from contaminants within the TNT itself. In Fig. 5 (right) no structure larger than the noise emerges from the baseline. The downward sloping of the baseline that was observed in this range in Fig. 4 is absent in Fig. 5 (right), suggesting that the broad features observed in Fig. 4 are artifacts. We note that the signal-to-noise ratio is worse than what would be necessary to observe the $\sim 0.5\%$ transmittance change due to an absorption with a reasonable cross section value of 10^{-18} cm^2 . Thus, the main value of Fig. 5 may be to emphasize that some combination of temperatures in excess of 40 C, path lengths longer than 10 m, and higher signal-to-noise ratio will be necessary for spectral sensing of TNT vapor below 100 cm^{-1} .

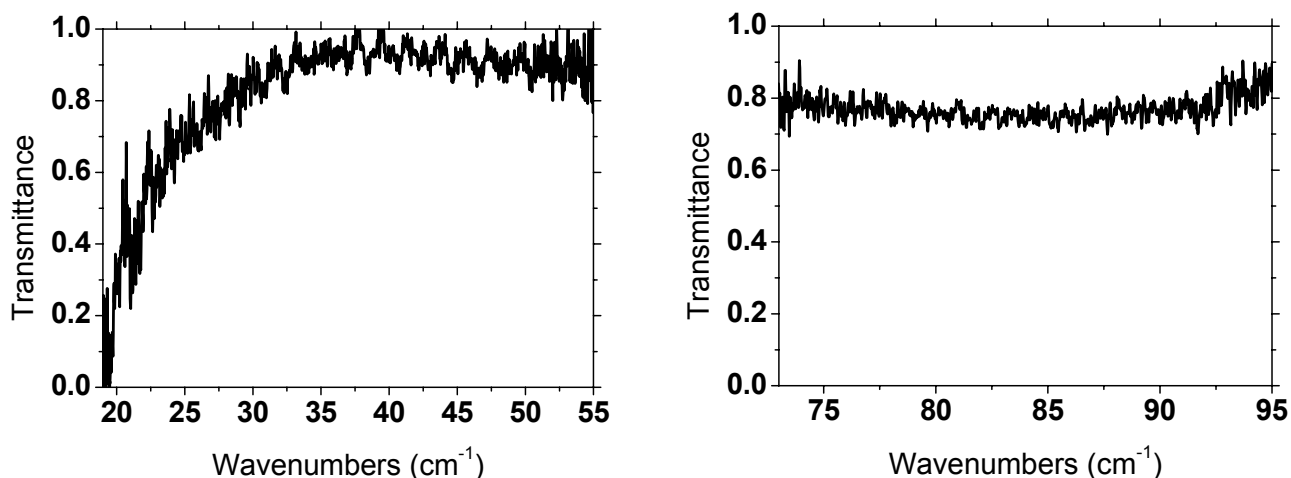


Fig. 5. Far-infrared spectrum for 10 m vapor cell containing TNT and heated to 40 C.

4. SUMMARY

Transmittance spectra of TNT solid has been measured in the range 30-660 cm^{-1} . Previously unreported lines were revealed. An attempt to measure the spectrum of TNT vapor in a 10 m cell heated to 40 C revealed absorption features that seem too strong to be attributable to TNT. This result suggests that higher temperature, longer path length, and higher signal-to-noise ratio will be necessary for sensing of TNT vapor in the THz frequency range.

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