

Terahertz (THz) spectroscopy of Freon-11 (CCl_3F , CFC-11) at room temperature

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Abstract

The rotational spectrum for the lowest vibrational mode for CCl_3F has been measured in the 0.1–2 THz frequency range using a compact time-resolved terahertz spectrometer. The peak of the population spectrum for the ground state rotational manifold was observed at 0.3 THz. The observed absorption profile was modeled with rotational and vapor pressure parameters. The limits of detectivity of the compact THz system are discussed in context of atmospheric sensing.

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1. Introduction

Trichlorofluoromethane (Freon-11, CFC-11, CCl_3F) has been one of the most widely used of the fully halogenated Chlorofluorocarbons (CFCs) in industrial applications. Since it is a chemically inert and non-toxic compound it has been extensively used as an aerosol propellant and refrigerant; however, its deleterious effects on the ozone layer in the stratosphere are now well understood [1]. The measurement of CFC concentration in the atmosphere remains of considerable interest and far-infrared spectroscopic methods will be useful for real-time investigation of such compounds [2].

The vibrational spectra of CCl_3F in the gaseous and liquid states have been extensively studied by both Raman [3] and infrared [4,5] techniques, and the normal modes have been well documented. The rotational spectrum due to the ground and low-lying vibrational states has also been studied [2,6,7]. In the mid-infrared region, the vibrational spectra of gases can be quite complex and even

harder to distinguish if multiple species are present in the sample being analyzed [8]. The use of rotational absorption signatures for detection or identification of gases is complementary to these more established techniques. Since almost all polar molecules exhibit rotational absorption lines from 0.1 to 6 THz [8], THz pulses can be used for their detection. In the past, in order to detect the individual rotational transitions, most techniques used harmonic-generation from klystrons to generate far-infrared light. This instrument typically requires meter-long pathlengths to obtain sufficient sensitivity to resolve rotational linewidths. In general, these experimental methods are limited to frequencies less than a few hundred gigahertz.

In order to gauge the concentrations of various volatile organic compounds (VOCs), current atmospheric research employs either collections from high-altitude observatories or sampling using high-altitude balloons from the upper troposphere to lower stratosphere. Typical concentrations for Freon-11 are on the order of 300 part per trillion by volume (pptv). In order to detect these levels atmospheric air samples are analyzed using a high-resolution gas chromatography method coupled with mass spectroscopy (GC/MS) [9]. While these measurements are invaluable for documenting the concentrations of VOCs in the

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atmosphere, a detailed picture of the concentration and distribution of these substances can be better obtained with fast optical methods.

In this Letter, we investigate the rotational spectrum of the ground state of CCl_3F above the GHz region using time-resolved terahertz spectroscopy (TRTS). By implementing a compact time-resolved THz spectrometer we discuss how ppmv to ppbv level of detection for Freon-11 can be achieved.

2. Methodology

Measurements were initially performed using a table-top THz system driven by an amplified Ti:Sapphire laser as described elsewhere [10]. The compact THz system we designed for the present study is driven by a mode-locked Erbium (Er):doped fiber laser (IMRA Inc., F-100 series laser) which has an average power of 100 mW at the frequency doubled output of $\lambda = 810$ nm, with a pulse width less than 150 fs at a repetition rate of 75 MHz (Fig. 1). After the light has passed a 50/50 beamsplitter, the visible beam, mechanically chopped at 3.5 kHz, is focused down to generate the THz pulses through optical rectification in a 2 mm thick ZnTe (110) crystal. The generated THz light is collimated using metallic parabolic reflectors to a diameter of 63.5 mm and focused on an identical ZnTe crystal, passing through collinear with the gating beam. Using phase-sensitive lock-in detection, changes in the polarization of the gating beam were detected with a balanced detector which had a gain of roughly 2000 V/A. The resulting set-up had a signal to noise (S/N) ratio better than 300, obtained by referencing the peak signal amplitude to the noise floor. The system is enclosed in a nitrogen-purged cage during scanning. The total THz path length is limited to the single-pass glass cell of 9.2 cm length

which was used to house the Freon-11 gas for measurements done with both the compact THz system as well as the table-top spectrometer.

The coherent THz transients obtained have a bandwidth from 0.1 to 2 THz, which is more than sufficient to study the rotational spectrum of a variety of chemical vapors. A THz pulse propagating through CCl_3F will be reshaped due to absorption and dispersion of the vapor. These changes are quantified by comparing the transmitted pulse to the reference pulse in the frequency domain, allowing for measurement of the real and imaginary index of refraction and finally the absorption coefficient of the sample.

At least 99% pure, liquid CCl_3F is purchased from Sigma–Aldrich (Product# 254991). 1 mL of the liquid is placed in the 9.2 cm long glass cell with a clear aperture of 5 cm. The windows consisted of 1 cm thick, 10 cm in length, polyethylene square slabs. Due to the low boiling point of CCl_3F (296.7 K) the sample is allowed to evaporate inside the closed cell at room temperature (300 K). The resulting pressure in the cell is approximately 220 torr (~ 300 hPa).

The time-domain reference and transmitted pulse obtained with the compact THz system is depicted in Fig. 2. Due to the back reflection from the ZnTe crystal the scans shown show only the portion up to 16 ps after the main pulse. After applying a numerical Fourier transform (FFT) to the time-domain data the absorption coefficient is obtained from the transmission (Fig. 3, the absorption spectrum obtained from the table-top system is shown in the inset figure).

3. Analysis

The broad absorption feature at low frequencies is due to the rotational spectrum of the ground state of CCl_3F ,

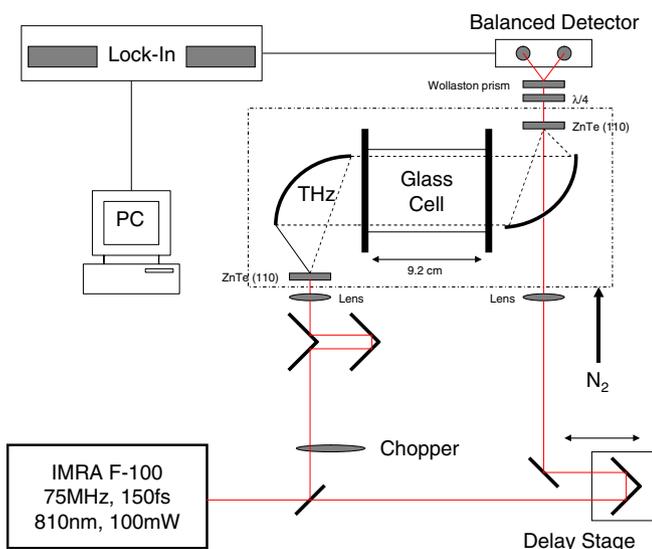


Fig. 1. Compact time-resolved THz spectrometer driven by a mode-locked Er: doped fiber laser. Glass cell is where the Freon-11 gas was housed.

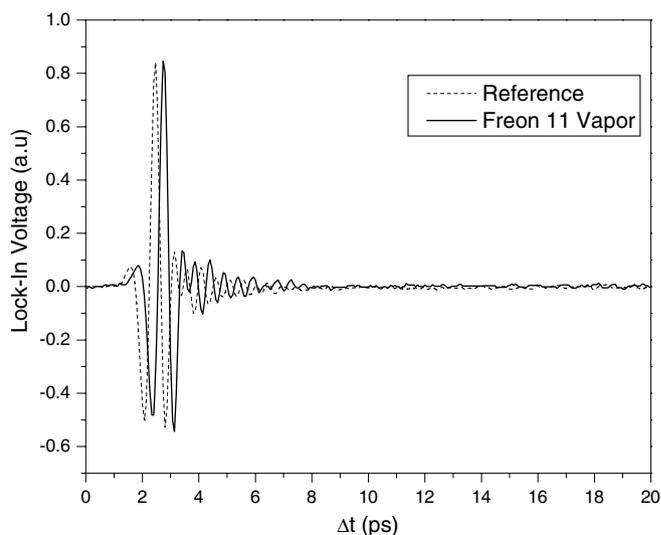


Fig. 2. Time-resolved THz scans of reference (dry N_2 purged empty cell) and CCl_3F vapor.

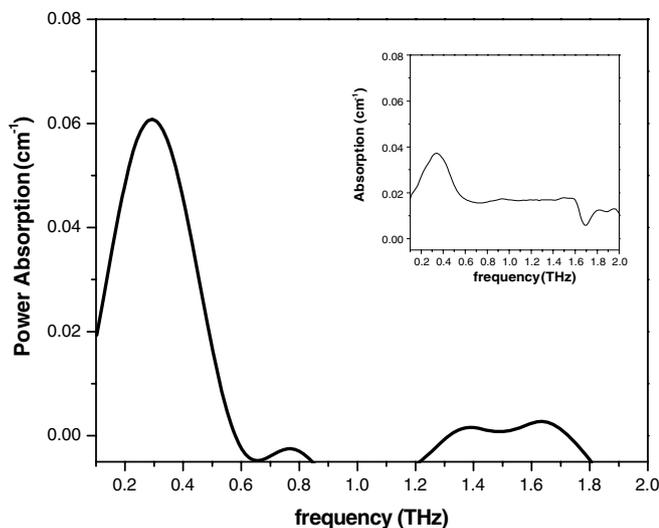


Fig. 3. Absorption spectrum for CCl_3F vapor through the 9.2 cm long gas cell using the compact THz system. The concentration of Freon-11 was on the order of part per thousand by volume. The broad absorption is due to the rotational transitions of the ground vibrational state. Inset figure was obtained with the table-top THz system.

since the 1st excited vibrational state lies at 241 cm^{-1} . These lines which originate from transitions between rotational quantum levels, can be theoretically modeled quite accurately [8,11]. To model the rotational absorption we use a method of analysis similar to Harde, Chevillie and Grischkowsky [12] based on the rotational absorption profile of a symmetric top molecule developed by Townes and Schawlow [13]. For CCl_3F , a symmetric top molecule, excitation of the molecular vapor by THz radiation induces transitions between pairs of J, K levels of the lowest vibrational state. For a molecule with such symmetry, there is no torque along the axis perpendicular to the symmetry axis. Since there are no angular momentum changes along that axis, only transitions from J, K to $J + 1, K$ will be observed. The absorption coefficient for such a transition can be calculated from:

$$\alpha_{JK}(\omega) = \omega C_{JK} g_x(\omega, \omega_{JK}), \quad (1)$$

where, $g_x(\omega, \omega_{JK})$ is a general absorption lineshape function of the form,

$$g_x(\omega, \omega_{JK}) = \frac{\Delta\omega_J}{(\omega - \omega_{JK})^2 + (\Delta\omega_J/2)^2} f_x^+ - \frac{\Delta\omega_J}{(\omega + \omega_{JK})^2 + (\Delta\omega_J/2)^2} f_x^-, \quad (2)$$

$\Delta\omega_J$ is the J -dependent FWHM angular frequency linewidth ($< 50\text{ GHz}$ [12]), and f_x^\pm is the shape factor which is 1 for a pure Lorentzian lineshape, while $f_x^\pm = \pm\omega/\omega_{JK}$ for a van Vleck–Weisskopf shape [14].

The transition frequencies can be obtained from the Hamiltonian of CCl_3F molecule as:

$$\omega_{JK} = 4\pi(J + 1)(B - D_{JK}K^2) - 8\pi D_J(J + 1)^3 \quad (3)$$

here, J is the rotational quantum number, B is the rotational constant [2,6,7], D_{JK} and D_J are the first order centrifugal distortion terms [2,6]. The coefficient C_{JK} is given by:

$$C_{JK} = \frac{\pi f_0 \mu^2}{3nc\epsilon_0 h} \cdot \frac{N_a p}{N_a kT + B'p} (1 - e^{-h\omega_{JK}/2\pi kT}) \times \left(J + 1 - \frac{K^2}{J + 1} \right) \frac{S(I, K)}{4I^2 + 4I + 1} \times \frac{hB}{kT} \sqrt{\frac{hA}{\pi kT}} e^{-h(BJ(J+1) + (A-B)K^2)/kT} \quad (4)$$

A is the rotational constant about the symmetry axis, p is the gas pressure, B' is the virial coefficient of a real gas ($-760.4\text{ cm}^3\text{ mol}^{-1}$), f_0 is the fraction of molecules in the

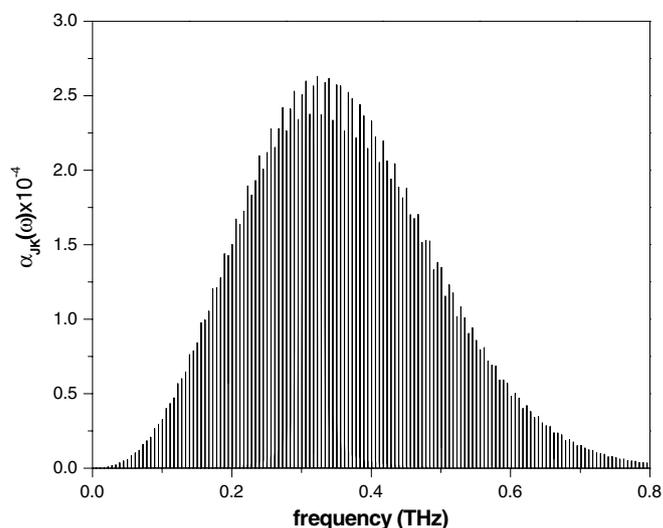


Fig. 4a. The rotational absorption calculated using Eqs. (1)–(4), for rotations involving quantum numbers J up to $J = 143$, and $K = 1$.

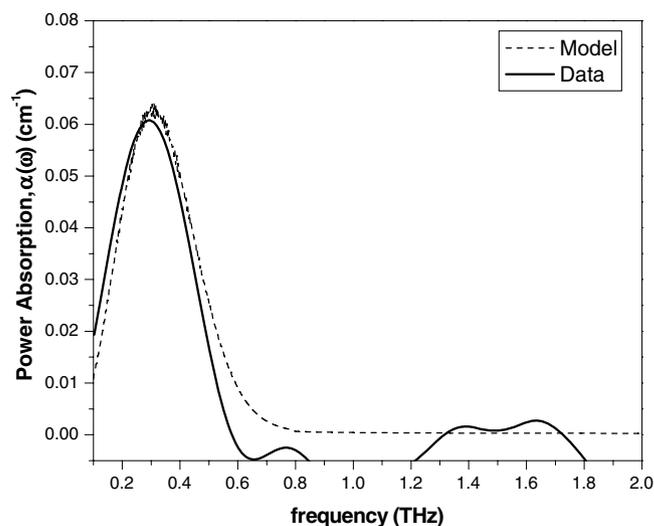


Fig. 4b. The absorption spectrum summed over all quantum numbers as given by Eq. (5) (solid line) and experimental absorption curve for comparison (dashed line).

lowest vibrational state (~ 1), μ is the electric dipole moment, $S(I, K)$ is the statistical weight of a J, K level, I is the nuclear spin of a chlorine atom, and N_a is Avagadro's constant.

The absorption over the spectral range of the THz pulse is found by summing over all rotational transitions:

$$\alpha(\omega) = \sum_K \sum_J \alpha_{JK}(\omega) \quad (5)$$

The calculated absorption coefficient, assuming a *van Vleck–Weisskopf* shape, is plotted against the observed absorption profile (Figs. 4a,4b).

4. Discussion

The far-infrared absorption spectrum of CCl_3F arise from rotational transitions due to its substantial dipole moment (0.450 Debye [15], e.g. (H_2O 1.85 D)). This suggests that we should observe strong dipole transitions in the THz spectrum. Other effects such as collision induced absorption can be safely neglected since it has a more significant role in molecules that do not have a permanent dipole moment [16]. The peak of the population spectrum for CCl_3F is located clearly below 15 cm^{-1} (Fig. 4b), as estimated from the absorption coefficient given by the coefficients C_{JK} , which is a function of the rotational constants, and the Boltzmann distribution. While we cannot resolve individual transitions which occur roughly on an interval equal to twice the rotational moment of inertia along the symmetry axis ($2 \times B$), the overall absorption profile for the majority of the rotational transitions of the ground state could clearly be observed. Since the peak of this manifold is dependent on the mass of the molecule, the absorption spectra for a mixture of polar molecules within a sample of air can be distinguished for a resolution as poor as 0.05 THz. This resolution allows for fast acquisition times since the THz waveforms can be limited to ~ 20 ps in the time-domain allowing for rapid scanning delay-stages.

Symmetric molecules like CCl_3F can also exhibit unique echoes which can only be measured with a time-domain method using THz pulses [17]. In the case of the symmetric rotor like CCl_3F , the regularly spaced rotational manifold will generate a series of recurrences or echoes of the initial pulse [18], at temporal delays that are multiples of the inverse of the rotational line spacing. The spacing between the echoes increases with increasing mass of the molecule, corresponding to the closer rotational line spacing in the frequency domain, thus the echoes of CCl_3F would occur at nearly 200 ps after the main pulse. Since we could not resolve the individual rotational transitions, we limited our scans for CCl_3F to about 16 ps after the main pulse. Recently, CH_3Cl was detected at the ppmv level by examining the echoes in the THz waveform by use of a THz white cell [19].

In the measurements discussed here the concentration of the CCl_3F is on the order of 1 part per thousand by volume, far below the goal of ppbv or pptv that is desirable

for atmospheric testing. To achieve the desired level of detection the THz beam must be guided over a longer path length. A well-collimated THz beam of ~ 1 cm radius can propagate for several meters before diffraction becomes significant [8]. These large beam diameters preclude the use of most commercially available White (multi-pass) cells, such as those used in many mid-infrared gas sensing systems. With a 4 m long multi-pass cell, ppmv level detection with our compact THz system is achievable. To reach the goal of ppbv resolution differential measurement techniques [20] are essential. With the development of higher power compact mode-locked fiber laser sources broadband THz systems are uniquely suited for in situ measurements of polar gas species.

5. Conclusion

The satisfactory agreement between the calculated and observed values for the absorption coefficient is a testament to the sensitivity of TRTS techniques. While individual rotational transitions are too narrow to be resolved due to the limit in our time-domain scans, the less than 10 cm pathlength at a molecular vapor concentration on order of part per thousand by volume was sufficient enough to resolve the rotational spectrum of the ground state of CCl_3F . Depending on the various molecule specific rotational parameters, the entire manifold of rotational lines for the ground state can be used as spectral markers to distinguish and identify various chemical species. With rapid development of compact broadband THz sources [21] as well as improved detection methods, portable instrumentation for the detection of aerosols and gases at the ppmv and ppbv levels are possible.

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