All Electronic THz Wave Absorption Spectroscopy of Volatile Organic Compounds Between 220-330 GHz

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***Abstract*—The rotational absorption spectra of important volatile organic compounds are characterized in the 220-330 GHz frequency band using a continuous-wave electronic THz spectrometer. Absorption spectra of a variety of pure volatile organic compounds are measured at controlled pressures, and the frequencies of the absorption lines agree with JPL's molecular spectroscopy database to within 30 MHz. The work presented here is a step towards size reduction of gas spectroscopy systems through miniaturization using standard silicon fabrication techniques, which would allow such systems to be used in the field for various industrial, environmental, and medical sensing applications.**

I. Introduction

Recent progress in high-performance microelectronic THz wave sources and receiver technologies is stimulating research on the development of electronic THz wave gas sensing systems [1], [2], [3]. The interest is driven by the envisioned impact of electronic THz wave sensing on, e.g., environmental monitoring, breath analysis, and industrial process monitoring [4]. THz wave absorption spectroscopy exploits the observation that the spectral selectivity of many relevant volatile organic compounds (VOCs) is higher for THz waves, compared to vibrational spectroscopy carried out in the infrared [5]. This helps with identifying individual molecular signatures from the spectrum of a mixture of multiple absorbers. Moreover, in the 220-330 GHz frequency band, the characteristic absorption spectra of VOCs interfere minimally with water vapor absorption and are unaffected by the presence of aerosols. Microelectronic-based THz sources and receivers are compact and have low power consumption in comparison to photonic systems and vacuum electronics [6]. These qualities are desirable for the development of THz rotational spectroscopy-based chemical sensors capable of operating in non-ideal environments.

In this paper, we report the absorption spectra of oxygenated hydrocarbons (alcohols, aldehydes, carboxylic acids, ketones), nitrogen-containing compounds (acetonitrile, nitromethane, nitrogen dioxide, nitric acid), and several halides (Cl-, I-, Br-containing) in the 220-330 GHz frequency band and identify rotational transitions. Most of the rotational transition frequencies for the asymmetrical VOCs are readily available using JPL's molecular spectroscopy database; however, for the halides and nitrogen-containing compounds, only chloromethane is documented. Where possible, transitions are identified by using their respective rotational constants in the rotational energy transition equation for a symmetric top molecule (eqn. 1). These constants are documented in [7] and [8] for chloromethane and iodomethane, respectively.

$$\Delta E(J,K) = E_{J+1,K} - E_{J,K} = 2B(J+1) - 4D_J(J^3 + 3J^2 + 3J + 4) - 2D_{JK}(J+1)K^2 \quad \textit{(eqn. 1)}$$

The rigid rotor model is a reasonable approximation for labeling the sparse rotational transitions of symmetric top molecules. These transitions are governed by the total angular momentum quantum number 'J'. When available, centrifugal distortion and coupling terms are also used to more accurately label transitions and include rotational transitions about the non-unique axes of the molecule, governed by the angular quantum number 'K'.

II. Results

A frequency-domain THz rotational spectroscopy system, similar to the one described in [1] and [2], is utilized to measure the absorption spectra of pure gases and mixtures of gases. Amplitude modulation is applied to the continuous signal of the THz source, and lock-in detection is used to extract the signal of interest from the detector output. For one experiment, two frequency sweeps are required: one, a baseline measurement with no absorbing gas, 'I_0', and the other, with the absorbing gas present, 'I'. Both sweeps are compared to determine the absorbance 'A', which has a linear relationship (for a fixed frequency of interrogating light) with the concentration 'c' and pathlength 'l' of the absorbing gas through the Beer-Lambert law.

$$A = -\ln\left(\frac{I}{I_0}\right) = \epsilon c l \quad \textit{(eqn. 2)}$$

The absorption coefficient 'ϵ' defines the absorption strength at the frequency of interest and the concentration and length terms simply scale the frequency-dependent absorption coefficient.

The frequency resolution of each experiment is governed by the frequency scan rate, lock-in averaging time (time constant), and the rate (frequency) of amplitude modulation. In the present experimental setup, we are limited by the THz source's on/off switching speed (can only modulate up to ~6 kHz) and the minimum averaging time on the lock-in amplifier. With these limitations, scan rates of 4-11 GHz/s were achieved, and a post-processing digital filter was implemented to clean up any high frequency electrical noise.

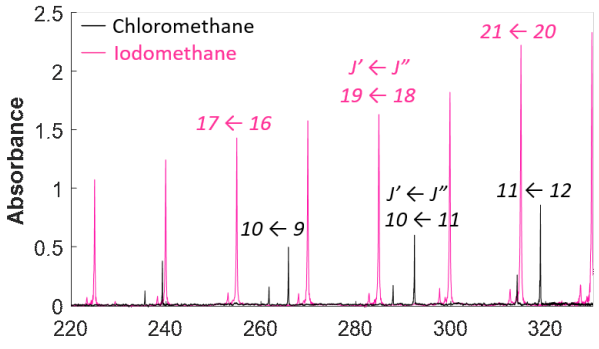

Fig. 1. Absorption for pure compositions of iodomethane and chloromethane at 1 Torr each.

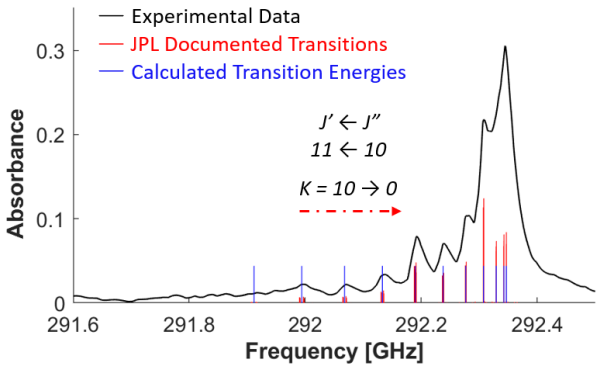

Fig. 2. Absorption for pure chloromethane at 0.25 Torr. The height representation of the JPL documented transitions are scaled from each transition's integrated intensity. The absolute value is arbitrary, and the relative scaling is simply for observation.

Spectral absorption measurements for the various compounds yielded unique spectra that are dependent on molecular structure. For example, experiments for halides yielded selective and distinct features that are attributed to the simplicity of their molecular structures, i.e., simple symmetric tops (CH_3-Halogen (prolate), or $C(Halogen)_3$-H (oblate)) (Fig. 1). Utilizing rotational constants and centrifugal distortion constants tabulated in [7], and [8] the line positions of the halides are confirmed and checked with JPL's molecular spectroscopy database [9] (Fig. 2). Here, the frequency resolution of the proposed scanning method is exhibited through the resolution of the individual rotational transitions for chloromethane (~40 MHz feature size), governed by the quantum number 'K' for each 'J'. Acetonitrile, a nitrogen-containing species, is another symmetric top with distinct and selective spectral characteristics (Fig. 4). On the other hand, oxygenated hydrocarbons, with asymmetric top geometries, yielded more complex spectra (Fig. 3). Although many transitions tend to overlap in the more complex spectra for asymmetric molecules, the sparsity of transitions in the frequency band of the present study allows for the separation of distinct spectral features for many oxygenated hydrocarbons (Fig. 5).

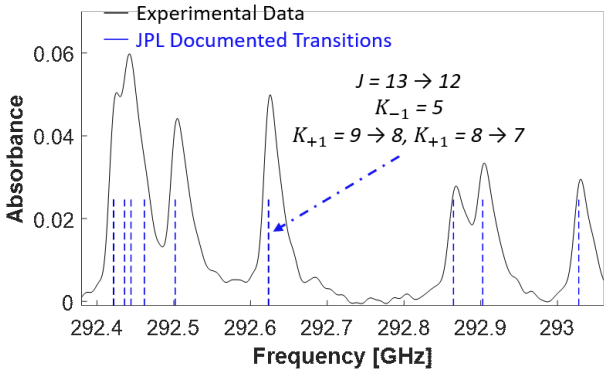

Fig. 3. Absorption for pure formic acid (asymmetric top) (zoomed in) at 1 Torr.

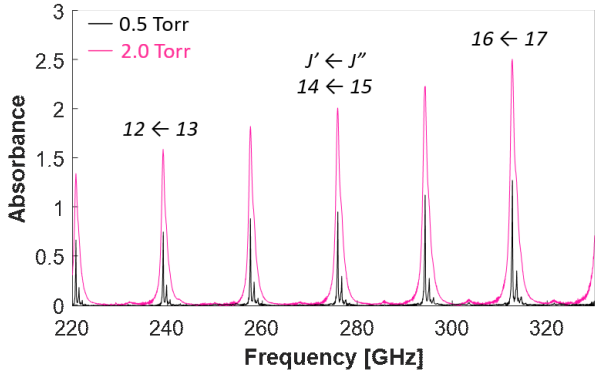

Fig. 4. Absorption for pure acetonitrile (symmetric top) at 0.5 and 2 Torr.

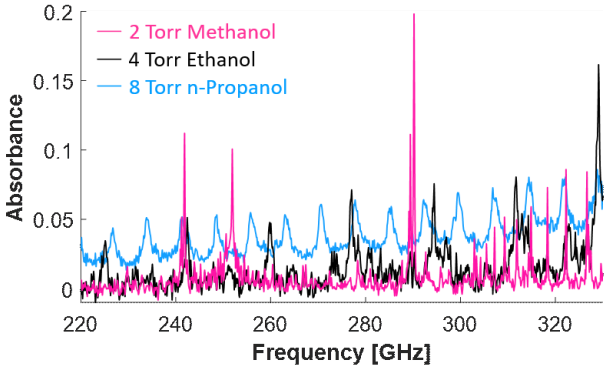

Fig. 5. Absorption for pure concentrations of alcohols.

III. Summary

We document the rotational absorption spectra for a variety of important VOCs (at least 16) in the 220-330 GHz bandwidth using a continuous-wave electronic THz spectrometer. Fast scan rates are achieved with certainty of line positions to within 30 MHz of the positions cataloged in the JPL molecular spectroscopy database. The results indicate that sensitive and selective gas sensing for VOCs in this frequency range is possible and can be developed using miniaturized microelectronics devices.

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