

SPECTRAL SIGNATURES OF ACETONE VAPOR FROM ULTRAVIOLET TO MILLIMETER WAVELENGTHS

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This paper presents comparative analysis of different wavelength ranges for the spectroscopic detection of acetone vapor. We collected and analyzed original absorption line spectra arising from electronic transitions in the ultraviolet, near-infrared vibrational overtones, mid-infrared fundamentals, THz torsional modes, and mm-wave rotational transitions. Peak absorption cross sections of prominent spectral features are determined. The relative merit of each spectral range for sensing is considered, taking into account the absorption strength, available technology, and possible interferences.

Keywords: acetone, vapor, millimeter waves, terahertz, infrared, overtone

1. Introduction

Development of sensitive spectroscopic techniques for acetone vapor detection has practical importance in pharmaceutical industry, medicine, security, terrorism prevention, global ecology monitoring, astrophysics, etc. Acetone C_3H_6O is an ingredient in Triacetone Triperoxide, or TATP, an exceptionally volatile explosive preferred by suicide bombers. TATP was used in the London subway bombings and as a trigger in the shoe bomb of Richard Reid. TATP is almost undetectable by conventional bomb detection systems, but of its base ingredients - drain cleaner, bleach and acetone - the latter has exceptionally high vapor pressure for a solvent. Thus, there is the possibility of detecting TATP and bomb manufacturing sites, by the presence of acetone vapor.

Detection of acetone vapor in human breath is of value as a screening diagnostic for diabetes^{1,2} and epilepsy³. Due to crude processing facilities, illicit cocaine usually

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contains trace amounts of solvents, including acetone, which might be a useful marker for drug enforcement efforts⁴. The pharmaceutical industry requires accurate determination of the amount of solvent removed during drying of drug substance and intermediates in paste, cake, or slurry forms⁵, and acetone is one of the major solvents used in drug manufacturing. Acetone exists in interstellar space because it is composed of only a few of the most abundant atoms. Detection requires accurate knowledge of the spectrum. The existence of interstellar acetone has been confirmed recently⁶.

Acetone has infinite solubility in water, which means that any sample of acetone exposed to air will have some dissolved water in it. Acetone's vapor density is twice that of air, so that the vapor tends to hug the ground. It has a vapor pressure of 181.7 Torr at 20 C, which is high compared with other solvents. Its vaporization rate at 20 C is 7.7, (i.e. it is large) compared to the value unity for butyl acetate.

The purpose of this paper is to compare absorption features of acetone vapor over a broad spectral range in order to be able to make some judgment about the relative merit of different spectral regions for acetone sensing. Absorption lines due to free rotations of the molecule are known at millimeter wavelengths⁷. At terahertz frequency, slow torsional motion of methyl groups are found^{8,9}. In the mid-IR occur the strong fundamental vibrations¹⁰⁻¹⁴, with overtones that have been studied to some extent throughout the near-IR and visible¹⁵⁻¹⁹. A strong electronic band is found in the near UV¹⁹. It is hoped that analysis and comparison in one paper of original spectroscopic data, collected with the application of sensing in mind, measured with high frequency accuracy, and with the determination of absorption cross sections, will enable new acetone detection methodologies.

2. Experimental methods

For millimeter wave spectroscopic studies of individual rotational lines of acetone, we used the method of non-stationary spectroscopy, namely the method of spectroscopy with phase switching of microwave radiation developed at the Institute for Physics of Microstructures²⁰. The spectrometer was based on a backward wave oscillator with radiation frequency stabilized by a phase lock-in circuit, which involves a harmonic mixer, a phase detector, and reference synthesizer. The backward wave oscillator used in this measurement was tunable in the range 115-185 GHz. Switching of the radiation phase is realized by means of 10 ns voltage pulses fed to the slow-wave structure of the BWO. The phase switched microwave radiation was fed through a 1 meter gas cell and detected by a Schottky-diode based detector. Typical phase switching repetition rate was 250 kHz. The method uses post-excitation coherent spontaneous response of excited gas molecules, which can provide sensitivity of spectroscopic detection of rotational lines with absorption level up to 10^{-9} cm⁻¹ with acquisition time of 1 second for a gas cell length of 1 meter. This method can be successfully used for detection of acetone

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concentration in human breath with limit 10^{-6} molar % at measurement acquisition time not more than several seconds²¹. Typical spectral shape of registered absorption line has Voigt form. Optimal level of gas mixture pressure for this method is 10^{-2} - 10^{-3} Torr, when the linewidth is below several MHz but above the Doppler limit. The method can have an accuracy of line central frequency determination as low 1 kHz, which provides unique identification of the gas being detected.

For wide range measurements of acetone vapor absorption spectra we used a vacuum-bench Bomem DA8 Fourier-transform spectrometer. The frequency range of the spectrometer extended from 20 cm^{-1} (0.5 mm wavelength or 0.6 THz frequency) through the visible with maximum resolution 0.04 cm^{-1} . For the range 20 - 55 cm^{-1} , a 50 micron thick mylar pellicle beamsplitter, a Hg arc source of black body radiation, and a 4 K Si bolometer (IR Labs) were used. For the range 40 - 200 cm^{-1} , the resources were changed to a 12 micron beamsplitter and a globar source. Spectra in the range 500 - 4000 cm^{-1} were collected using a Ge-coated KBr beamsplitter and HgCdTe detector. From 4000 - 14000 cm^{-1} , a quartz-halogen lamp, a quartz beamsplitter, and a liquid-nitrogen cooled InSb detector were used. From 8500 to 25000 cm^{-1} , a Si detector was used. The spectrometer optics and sample compartments were evacuated to a pressure of ~ 100 mTorr. Transmittance spectra were calculated as a ratio of the sample and reference spectra. Depending on the expected strength of acetone absorption lines in each spectral range, a 10 cm long stainless-steel cell with polyethylene or KBr windows, or a 10 m multi-pass White cell with polyethylene or quartz windows, was used to contain the vapor sample. Either cell can be contained completely within the evacuated spectrometer sample compartment. A reference spectrum was collected while the cell was continuously evacuated to a pressure of 70 mTorr. For identification of atmospheric absorption features due to water vapor, transmittance spectra of laboratory air and outdoor air were also collected.

The UV absorption spectrum of acetone vapor was measured by a Varian spectrometer with 10 cm gas cell and KBr windows, which provided reasonable transparency at wavelengths longer than 200 nm. Transmittance was calculated as a ratio of the sample spectrum and reference spectrum.

3. Results

3.1. Millimeter waves

Fig. 1 presents absorption spectra of acetone vapor near 132 GHz measured at gas pressure 20 mTorr. The line shape on the figures represents the second derivative of the natural absorption line. Due to absence of other gases in these measurements the spectra were collected during a single sweep of the frequency with sufficient signal-to-noise ratio. The signal-to-noise ratio can be remarkably improved by multi-scan data acquisition with averaging, while detecting weak lines or situations with low partial

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concentrations. The value of the absorption cross section for the line at 132.010 GHz is $3.8 \times 10^{-20} \text{ cm}^2$.

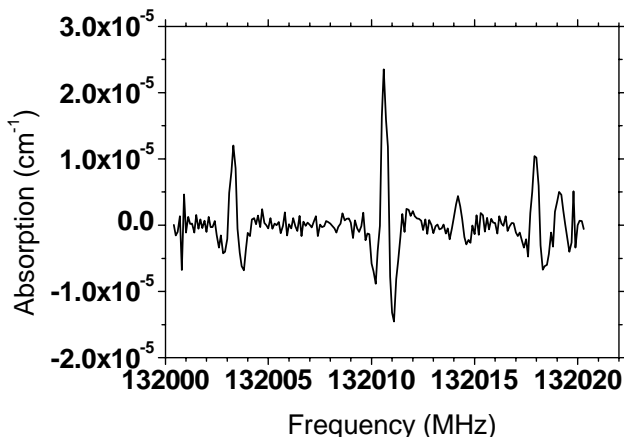


Fig. 1. High-resolution mm-wave spectrum of acetone vapor at a pressure of ~20 mTorr.

3.2. Low THz range

Fig. 2 presents the low terahertz spectrum collected using the Fourier spectrometer at resolution $0.04 \text{ cm}^{-1} = 1.2 \text{ GHz}$. This resolution is too coarse to resolve individual absorption lines as in Fig.1, so the spectrum appears as a wide band. For comparison, the spectrum of methanol, collected for the same spectral range, path length, and resolution, showed strong characteristic structure, which can be expected since methanol has a smaller moment of inertia, giving rise to larger separation of the main groups of rotational transitions²². We identify all sharp lines in Fig. 2 as being due to water vapor, which originates from the liquid acetone source itself.

From the 0.4 Torr spectrum, a peak absorption cross section of $1.2 \times 10^{-19} \text{ cm}^2$ is estimated at 0.7 THz. This value is large compared to the cross sections of acetone lines in other spectral regions. Thus, apart from the absence of resolvable structure at atmospheric pressure, and due also to a comparative lack of interferences from water vapor or other ambient molecules, the spectral range below about 30 cm^{-1} (beyond about 0.33 mm wavelength) appears to be an attractive region for acetone sensing.

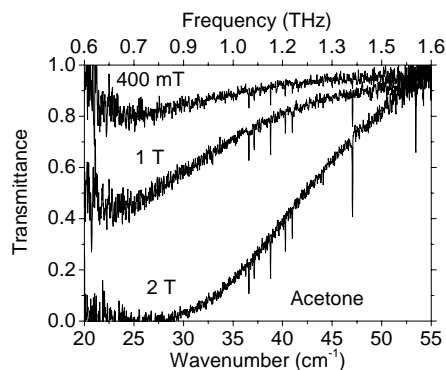


Fig. 2. Low THz spectrum of acetone vapor at three different pressures. The optical path length was 10 m and the spectral resolution was 0.04 cm⁻¹.

3.3. Mid THz range

In the mid-THz range the problem of intrinsic water-vapor absorption emerges and starts to dominate the spectrum above 50 cm⁻¹. All water lines in our spectra arise from the liquid acetone source itself, since we find that the residual water absorption in the evacuated spectrometer bench divides out quite well in the calculated transmittance. The mid-THz spectrum is presented in Figs. 3 and 4. For these measurements, the acetone pressure was 23 Torr, the spectral resolution was 0.25 cm⁻¹, and the optical path length was 10 m. The 40-200 cm⁻¹ range of the collected data overlaps with the low-THz spectrum of Fig. 2. The broad increase of the absorption below 70 cm⁻¹ in Fig. 3 is due to acetone and corresponds to the same absorption increase observed in Fig. 2 below 55 cm⁻¹. The absorption band is stronger, wider, and extends to higher wavenumbers in Fig. 3 because of the higher acetone concentration in this experiment. All of the sharp lines in Fig. 3 are due to water vapor.

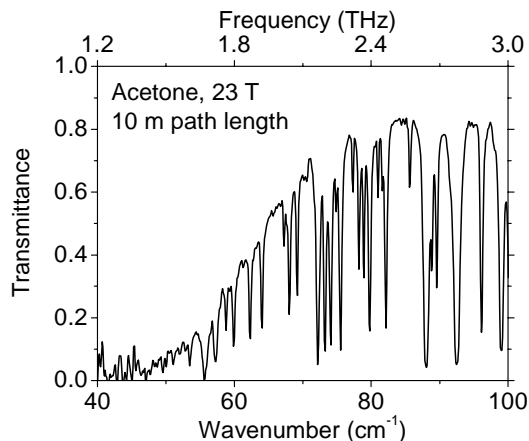


Fig. 3. Mid-THz spectrum of acetone vapor. The spectral resolution was 0.25 cm⁻¹.

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The spectrum in Fig. 4 extends the range of Fig. 3 up to 130 cm^{-1} . The two marked lines in Fig. 4 are identified as belonging to acetone by comparison with a water absorption spectrum, and these have been identified previously as torsional modes^{8,9}. In Ref. [8], the acetone pressure was its saturated value 181.7 Torr and the spectral resolution was 0.1 cm^{-1} . Compared with Ref. [8], the water lines in Figs. 3 and 4 are stronger relative to the acetone lines, but this better represents the likely situation one would encounter in field sensing.

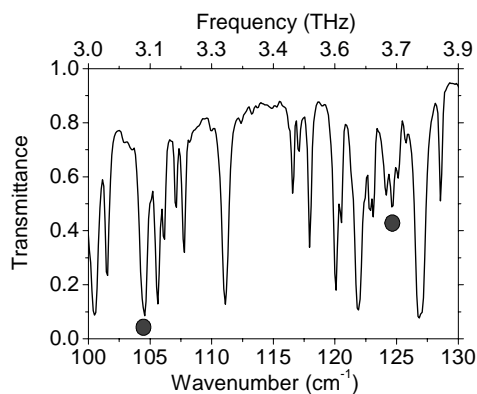


Fig. 4. Mid-THz spectrum of acetone vapor with torsional modes indicated by symbols. The acetone vapor pressure was 23 Torr, the optical path length was 10 m, and the spectral resolution was 0.25 cm^{-1} . All other lines are due to water vapor.

One of the marked absorption bands, a triplet, occurs at 124.6 cm^{-1} in the gap between water lines. Calculations⁹ have identified this band as the fundamental for methyl-group rotation clockwise-counterclockwise torsion mode $\nu = 0(\text{G}) \rightarrow \nu = 1(\text{G})$. Four transitions are expected here within a 2.2 cm^{-1} wide range. In the previous study⁸, at the saturated vapor pressure of acetone 181.7 Torr, none of these transitions were clearly resolved, even at a spectral resolution of 0.1 cm^{-1} .

The other acetone transition identified in Fig. 4 at 104.6 cm^{-1} is identified as the first sequence transition $\nu = 1(\text{G}) \rightarrow \nu = 2(\text{G})$, and is expected to be a 4 line multiplet spread over a range of 3.38 cm^{-1} . None of this is clear in Fig. 4, because these transitions exactly coincide with a water band. The presence of an acetone band here is verified in our work only by an increase in strength of the 104.6 cm^{-1} line relative to the other water lines when acetone vapor is in the cell.

The second sequence torsional transition $\nu = 2(\text{G}) \rightarrow \nu = 3(\text{G})$ was predicted to occur at 139 cm^{-1} , and from the discrepancy between theory and experiment for the two bands already discussed, one might expect a band to appear at $132 \pm 4\text{ cm}^{-1}$. Such a band remains undiscovered: We find nothing attributable to acetone in the range $130\text{-}200\text{ cm}^{-1}$. We collected no data in the range $200\text{-}490\text{ cm}^{-1}$.

Both torsional bands in Fig. 4 are well within the tuning range of the p-Ge laser²³, or within the range for which quantum cascade lasers can be made²⁴. However, the absorption cross section of the band at 124.6 cm^{-1} is only about $6.3 \times 10^{-22}\text{ cm}^2$. Given the smallness of this cross section, the strong interferences from the overlapping bands of water vapor, the lack of resolved characteristic structure at atmospheric conditions, and the paucity of other characteristic lines in this spectral range, the mid-THz appears to be a particularly poor region for sensing of acetone vapor.

3.4. Mid-IR range

The mid-IR spectrum of acetone is well known. We performed our own measurements over the range $490\text{ to }4000\text{ cm}^{-1}$, but we present only a sampling of it here in order to make a point about sensing and the competition with water vapor absorption. (Our results for the entire mid-IR spectral range are summarized at the end of the paper.) Fig. 5 presents the acetone vapor spectrum from $1165\text{ to }2000\text{ cm}^{-1}$. Very strong lines are observed at $1215, 1363, \text{ and } 1731\text{ cm}^{-1}$. The first (C-C asymmetric stretch) at $8.23\text{ }\mu\text{m}$ is a potential candidate for sensing due to the availability of commercial quantum cascade lasers [2] and because it falls in a region of relatively low water vapor absorption. The fine structure between the higher two lines is water vapor. These higher two lines have been considered poor candidates for open path sensing because of competition with water vapor [14], but we note that the Fig. 5 sample has the same water content as in Fig. 4, while the water vapor interference in Fig. 4 is comparatively minor. Moreover, even the weakest barely-visible feature at $\sim 1530\text{ cm}^{-1}$ in Fig. 5 has a cross section that is more than twenty times larger than that for any of the THz torsional transitions in Fig. 4.

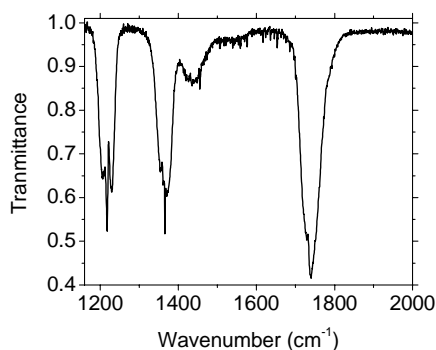


Fig. 5. Acetone vapor spectrum in the range from $8.6\text{ to }5\text{ }\mu\text{m}$. The acetone pressure was 6 Torr, the optical path length was 10 cm, and the spectral resolution was 1 cm^{-1} .

Fig. 6 presents the acetone vapor spectrum in the range $2750\text{ -- }3600\text{ cm}^{-1}$. The strong C-H mode at 2972 cm^{-1} ($3.36\text{ }\mu\text{m}$) is a potentially interesting signature for sensing,

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because it is in a region of low atmospheric absorption, and because a HeNe laser line falls within the band.

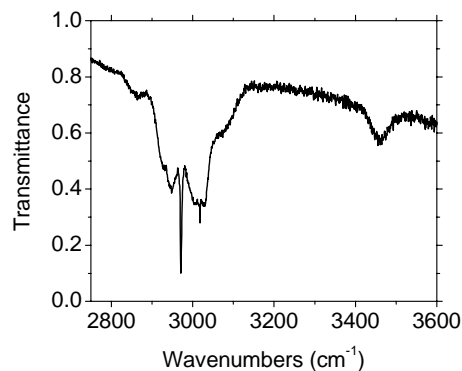


Fig. 6. Acetone spectrum in the wavelength range 3.6 to 2.8 μm . The acetone pressure was 51 Torr, the optical path length was 10 cm, and the spectral resolution was 1 cm^{-1} .

3.5. Near-IR range

Near-IR overtone bands below 3 μm wavelength can be beneficial for spectroscopic sensing due to the availability of many near-IR solid-state laser lines and high atmospheric transparency. We were able to measure near IR overtones throughout the wavenumber range 4000 to 15000 cm^{-1} , but only a sample is presented here with cross sections for all of them summarized at the end. Fig. 7 presents the transmittance spectrum in the range 5000-6250 cm^{-1} . At least 5 transitions attributable to acetone are distinguished. A band of water vapor interference occurs in the range 5160-5540 cm^{-1} . The peak frequencies of the observed lines are 5163*, 5635*, 5766*, 5915, 5980*, and 6063 cm^{-1} . Asterisks indicate the existence of coincident solid-state laser lines²⁵.

Use of near-IR cavity ring down spectroscopy to detect the presence of acetone has recently been suggested¹⁹. Ref. [19] presented a spectrum of the absorption cross section for a single near-IR absorption line around 6000 cm^{-1} using a tunable external-cavity diode laser and cavity ringdown system. The spectral range of this laser was limited to 5952-6135 cm^{-1} , and the spectrum produced is plotted as symbols in the Fig. 7 insert together with our data¹⁹. (The symbols are transmittance values calculated for our experimental conditions from the absorption cross section data presented in Ref. [19].) On the vertical scale, the two sets of data are in good agreement, so that we can simply cite Ref. [19] for the cross section of the deepest line as having the value $1.2 \times 10^{-21} \text{ cm}^2$. On the other hand, there is a 20 cm^{-1} discrepancy in the frequency position of this line¹⁹. Since a Fourier spectrometer determines wavenumbers by counting zero-crossings for the interferogram of a stabilized single-mode HeNe laser during the scanning of a Michelson interferometer, we believe that the absolute frequency accuracy of our data is higher than that of Ref. [19], which used a tunable laser. The discrepancy serves to highlight one of

the main challenges to sensing of even so common a vapor as acetone, namely, the low accuracy of frequencies for sharp characteristic absorption lines found in the literature.

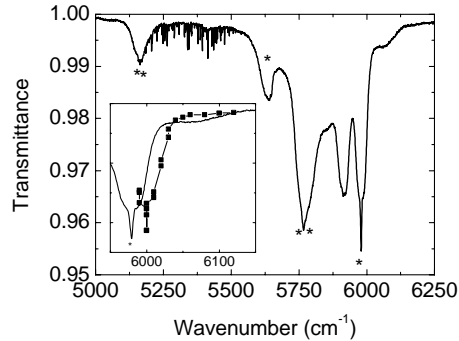


Fig. 7. Transmittance spectrum of acetone vapor in the wavelength range 1.60 to 2.00 μm , which corresponds to the $\Delta\nu_{\text{CH}} = 2$ overtone[16]. The optical path length was 10 cm, the acetone pressure was 122 Torr, and the resolution was 1 cm^{-1} . The inset shows an expanded region where previously published spectral data exist (symbols, Ref. [19]). Asterisks indicate the existence of solid state lasers at those wavenumber positions.

3.6. UV Range

The UV spectrum of acetone vapor is well known, so there is no need to present our spectrum here. The value¹⁹ of the cross section at its 265 nm peak is $\sim 4.5 \times 10^{-20} \text{ cm}^2$. This value, while a factor ~ 10 lower than the strongest mid-IR line, is still sufficient to make the UV range useful for detection of concentrations as low as $\sim 500 \text{ ppb}$ ¹⁹. Strong Doppler broadening, however, makes the UV line broad and featureless, such that it may be difficult to distinguish acetone from other UV absorbing vapors.

4. Discussion and Summary

From the transmittance spectra T we determined the absorption coefficient $\alpha = -(1/d) \ln(T)$, according to Beer's law. Absorption cross sections σ are determined from α according to $\sigma = \alpha/n$, where $n = P/kT$ is the number density, P the pressure, k Boltzmann's constant, and $T = 296 \text{ K}$ the temperature of the vapor. Peak cross sections of the strongest absorption lines in each of the major spectral groups studied here are presented in Fig. 8.

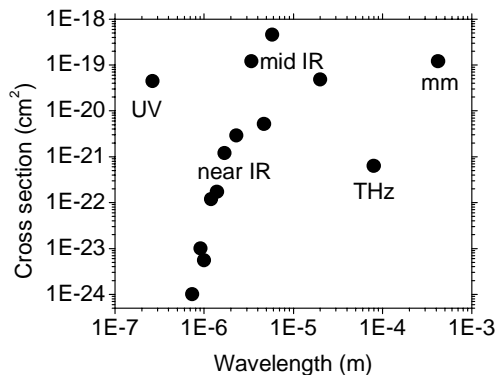


Fig. 8. Log-log plot of experimental peak absorption cross-sections for strong lines of acetone vapor in each spectral range studied vs. wavelength.

The mm-wave spectral region has the largest number of characteristic transitions upon which to base an acetone sensing methodology, but the vapor must be at pressure on the order of tens of mTorr in order for these lines to be well resolved. The mid-IR spectral region has 4 very strong lines, two of which fall within atmospheric transparency regions and are thus good candidates for open path work. Although the near-IR overtones are weaker, they coincide with known solid state laser transitions where the atmosphere is also quite transparent. The UV absorption cross section is rather strong, but the absorption spectrum is very wide due to strong Doppler broadening at high frequencies, and thus may not be sufficiently characteristic of the molecule. By far the worst region for sensing is the mid-THz range, where the acetone lines are weak, while the water vapor spectrum is densely populated with strong lines.

5. References

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