

Terahertz spectroscopy of acetone vapor

R. E. Peale, A. V. Muravjov, J. W. Cleary, T. Brusentsova, C. J. Fredricksen, G. D. Boreman

Physics Department and College of Optics and Photonics, University of Central Florida, Orlando FL 32816, 407 823 5208, FAX: 407 823 5112, rep@physics.ucf.edu

V. L. Vaks, A. V. Maslovsky, S. D. Nikifirov

Institute for Physics of Microstructures, RAS, Nizhny Novgorod, GSP-105, 603950, Russia

Abstract: Original terahertz spectra of acetone vapor-phase vibrational, torsional, and rotational transitions determine peak absorption cross sections for sensing applications.

©2006 Optical Society of America

OCIS codes: (300.6390) Spectroscopy, molecular; (300.6270) Spectroscopy, far infrared

Development of sensitive spectroscopic techniques for acetone vapor detection has practical importance in pharmaceutical industry, medicine, security, global ecology monitoring, and astrophysics. Acetone C_3H_6O is an ingredient in Triacetone Triperoxide, or TATP, an exceptionally volatile explosive preferred by suicide bombers that is almost undetectable by conventional bomb detection systems. 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 epilepsy [3]. Due to crude processing facilities, illicit cocaine usually contains trace amounts of solvents, including acetone, which might be a useful marker for drug enforcement efforts [4]. The pharmaceutical industry requires accurate determination of the amount of solvent removed during drying of drug substance and intermediates in paste, cake, or slurry forms [5], and acetone is one of the major solvents used in drug manufacturing. Acetone exists in interstellar space [6] because it is composed of only a few of the most abundant atoms. Detection requires accurate knowledge of the spectrum. The purpose of this paper is to compare absorption features of acetone vapor over a broad range of THz wavelengths to evaluate the potential of this region for acetone sensing.

For millimeter-wave spectroscopy of individual rotational lines, non-stationary spectroscopy with phase switching of microwave radiation [7] was used. The spectrometer is based on a backward wave oscillator, frequency stabilized by a phase lock-in circuit that includes a harmonic mixer, a phase detector, and reference synthesizer. Data was collected in the range 115-700 GHz. Phase switched is realized by 10 ns ~250 kHz voltage pulses fed to the slow-wave structure of the BWO, whose radiation is then fed through a 1 meter gas cell and detected by a Schottky-diode detector. 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 concentration in human breath with limit 10^{-6} molar % at measurement acquisition time not more than several seconds [8]. Spectral line shapes are Voigtian. Optimal vapor pressure is 1 to 10 mTorr, where 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.

A vacuum-bench Bomem DA8 Fourier-transform spectrometer was used to obtain transmittance spectra in the range 0.6 to 60 THz with a recently-upgraded maximum resolution 0.017 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. In the range 200-600 cm^{-1} , a 3 micron pellicle and globar source were 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. A 10 m multi-pass White cell with polyethylene was used to contain the vapor sample. This cell was contained completely within the evacuated spectrometer sample compartment. Reference spectra were collected while the cell was continuously evacuated to a pressure of 70 mTorr.

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 concentrations. The value of the absorption cross section for the line at 132.010 GHz is $3.8 \times 10^{-20} \text{ cm}^2$. The lines become undetectable by this method at pressures above 500 mTorr.

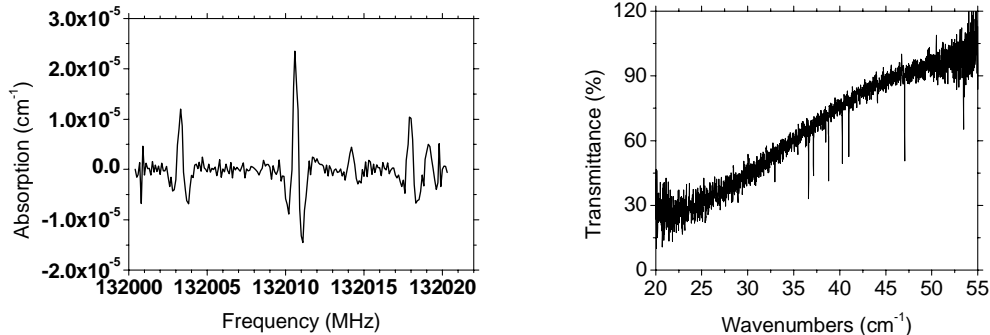


Fig. 1. (left) High-resolution mm-wave spectrum of acetone vapor at a pressure of ~20 mTorr.

Fig. 2. (right) Low THz spectrum for acetone pressure of 1 Torr, optical path length 10 m, and resolution 0.017 cm^{-1} .

Fig. 2 presents a transmittance spectrum in the range 0.6 to 1.65 THz. All sharp lines are due to water vapor, which originates from the liquid acetone source itself. The high resolution of $0.017 \text{ cm}^{-1} = 0.5 \text{ GHz}$ is nevertheless still too coarse to resolve individual rotational absorption lines acetone, so that its spectrum appears as a broad band. A fairly large peak absorption cross section of $1.2 \times 10^{-19} \text{ cm}^2$ is estimated at 0.7 THz, which together with a comparative lack of water vapor interference suggests that the spectral range below about 1 THz is attractive for sensing. No acetone absorption is detected in the range $55\text{-}100 \text{ cm}^{-1}$ (1.65-3.0 THz).

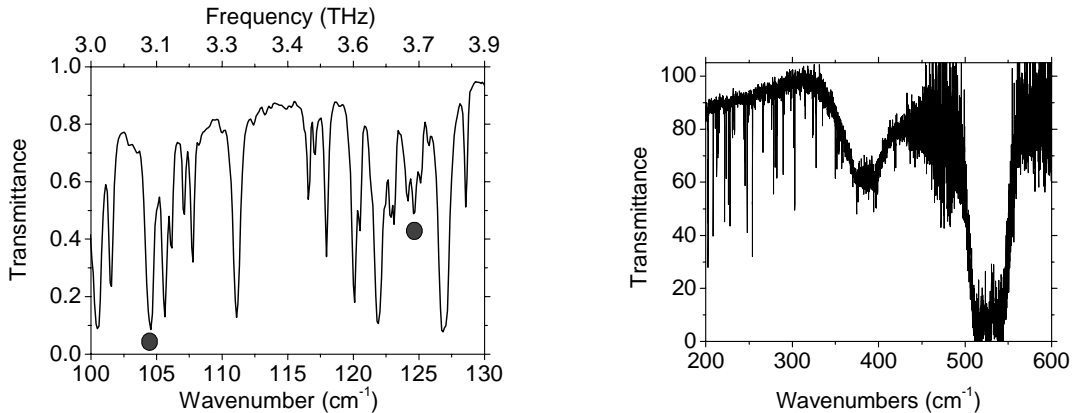


Fig. 3. (left) Mid-THz spectrum of acetone vapor with torsional modes indicated by symbols. The acetone vapor pressure was 23 Torr, the optical path length was 10 m, and the spectral resolution 0.25 cm^{-1} . All other lines are due to water vapor.

Fig. 4. (right) Acetone vapor spectrum in the range from 6 to 18 THz. The acetone pressure was 1.2 Torr, the optical path length 10 m, and the spectral resolution 0.1 cm^{-1} .

A mid-THz spectrum in the range $100 - 130 \text{ cm}^{-1}$ ($3.0 - 3.9 \text{ THz}$) is presented in Fig. 3, where the two marked lines are identified as due to acetone by comparison with a spectrum of air. These two bands are acetone torsional modes [9,10]. All other lines are due to water vapor 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. One of the marked absorption bands, a triplet, occurs at 124.6 cm^{-1} in the gap between water lines. The other acetone transition at 104.6 cm^{-1} exactly coincides with a water band. The presence of an acetone band here is verified by a doubling in strength of the 104.6 cm^{-1} line relative to the other water lines when acetone vapor is in the cell. 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.

We find nothing attributable to acetone in the range 130-200 cm^{-1} , but two broad strong bands appear in the range 200-600 cm^{-1} (Fig. 4). The signal-to-noise ratio becomes poor in the high range of this spectrum due to the decrease in beamsplitter modulation efficiency, but the 100% deep band there is nevertheless quite clear. For the weaker line near 380 cm^{-1} (11.4 THz), the peak absorption cross section can be estimated as $4.2 \times 10^{-19} \text{ cm}^2$, which is up to 1 order larger than the cross sections below 1 THz and 3 orders larger than the values for the torsional lines. Moreover, the water vapor interferences appear to be dying out above 350 cm^{-1} .

In summary, the mm-wave spectral region up to ~1 THz has the largest number of characteristic transitions and weak water interference, but the vapor pressure must be low to avoid pressure broadening. The mid-THz range is poor for sensing because lines are very weak while the water interference is very strong. The high-THz vibrational transitions have strong cross sections, relatively weak water vapor interference, and their lineshapes should change little with pressure, but the large widths may hinder sensing specificity.

References

1. A. Manolis, The diagnostic potential of breath analysis, *Clin. Chem.* 29(1), 5-15 (1983).
2. J. Donohue, K. O'Dwyer, B. D. MacCraith, C. Charlton, B. Mizaikoff, Quantum cascade laser-based sensor for monitoring physiological indicators in human breath, Europt(r)ode VII, 4-7 April 2004, Madrid, Spain.
3. K. Musa-Veloso, E. Rarama, F. Comeau, R. Curtis and S. Cunnane, Epilepsy and the Ketogenic Diet: Assessment of Ketosis in Children Using Breath Acetone, *Pediatric Res.* 52(3), 443-448 (2002).
4. W. H. Soine, Contamination of clandestinely prepared drugs with synthetic by-products, *NIDA Res. Monogr.* 95, 44-50 (1989).
5. S. C. Harris and D. S. Walker, Quantitative real-time monitoring of dryer effluent using fiber optic near-infrared spectroscopy, *J. Pharm. Sci.* 89(9), 1180-1186 (2000).
6. L. E. Snyder, F. J. Lovas, D. M. Mehringer, N. Y. Miao, Y-J. Kuan, J. M. Hollis, and P. R. Jewell, Confirmation of Interstellar Acetone, *Astrophysical J.* 578, part 1, 245-255(2002).
7. V. L. Vaks, A. B. Brailovsky, V. V. Khodos, Millimeter range spectrometer with phase switching – novel method for reaching of the top sensitivity, *IR & mm waves* 20(5), 883-896 (1999).
8. V. L. Vaks, N. V. Klyueva, Microwave spectroscopy of nitric oxide in exhaled air, *Proc. 17th Intl. Conf. High Resolution Molecular Spectroscopy, Prague, Czech Republic, September 1-5 (2002)* p. D22.
9. P. Groner, G. A. Guirgis, J. R. Durig, Analysis of torsional spectra of molecules with two internal C3v rotors. XXIV. High resolution far infrared spectra of acetone-d0, -d3, and -d6, *J. Chem Phys.* 86(2), 565-568 (1987).
10. Y. G. Smeyers, M. L. Senent, V. Botella, D. C. Moule, An ab initio structural and spectroscopic study of acetone- An analysis of the far infrared torsional spectra of acetone -h6 and -d6, *J. Chem. Phys.* 98(4), 2754-2767 (1993).