



Infrared absorption cross-sections for acetaldehyde (CH₃CHO) in the 3 μm region

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ABSTRACT

A series of infrared absorption cross-sections for acetaldehyde has been measured in the 3 μm region from spectra obtained using a high-resolution Fourier transform spectrometer (Bruker IFS 125/HR). Results presented are for mixtures of acetaldehyde vapor combined with pure synthetic air taken at various temperatures and pressure to simulate atmospheric conditions found principally in the Earth's troposphere and lower stratosphere. Spectra were recorded at a resolution of 0.005 cm⁻¹ and intensities were calibrated using three acetaldehyde spectra (measured at 278, 298 and 323 K) provided by the Pacific Northwest National Laboratory (PNNL) IR database.

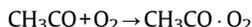
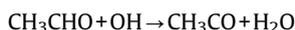
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1. Introduction

Acetaldehyde (CH₃CHO) is a trace molecular species found in the Earth's atmosphere. It plays an important role in the atmosphere as a source of ozone (O₃), peroxyacetyl nitrate (PAN) and HO_x radicals. Sources for acetaldehyde are primarily from photochemical production (estimated as 128 Tg yr⁻¹), with the oxidation of hydrocarbons (alkanes, alkenes and ethanol) as its main source [1,2], followed by biogenic emission from plant decay (23 Tg yr⁻¹) with anthropogenic combustion (2 Tg yr⁻¹) and biomass burning (3 Tg yr⁻¹) as lesser contributors [1].

The global atmospheric lifetime of acetaldehyde is less than one day (approx. 10–20 h) due principally to rapid oxidation by hydroxyl radicals [1,3]. Other sinks include photolysis as well as wet and dry deposition [1]. Acetaldehyde has a rather short lifetime in the boundary layer, but free tropospheric concentrations are on the order of 200 ppt. The distribution of acetaldehyde in the atmosphere is localized near its sources and is predominantly found from the equator to mid-latitudes, concentrated over

the continental land masses. When acetaldehyde reacts with the hydroxyl radical, OH removes H to form CH₃CO, which adds oxygen to yield the acetylperoxy radical, CH₃CO · O₂ [4]:



This radical can then react with NO₂ to form PAN (CH₃CO · O₂NO₂), and also serves as a precursor in the formation of O₃ and HO_x.

As a short-lived oxygenated volatile organic compound (OVOC) that is generated from the combustion of biomass, acetaldehyde is potentially an important marker species for identifying young biomass burning plumes. The Atmospheric Chemistry Experiment (ACE), on-board the Canadian satellite SCISAT-1, uses a high-resolution Fourier transform spectrometer (FTS) for remote sensing of the limb of the Earth's atmosphere down to 5 km. The ACE-FTS has wide spectral coverage in the infrared covering a continuous region from 750 to 4400 cm⁻¹ [5] and currently offers, through the current Version 3.0 data set (<http://www.ace.uwaterloo.ca>), retrievals for 38 molecular

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species (as well as their isotopologues), over a dozen of which are known tracers of biomass burning. Several previous studies have been conducted using ACE to examine biomass burning emissions [6–9], with more studies currently underway. We hope to include additional VOC and OVOC species such as acetaldehyde to be retrieved by ACE-FTS to aid in plume characterization.

Also of interest, Lewis et al. [2] have noted a curious aspect in the atmospheric distribution of acetaldehyde. Although acetaldehyde has a lifetime of < 1 day and atmospheric concentrations are generally localized near their emission sources, elevated levels of acetaldehyde were found over the North Atlantic ocean. It is speculated that since photochemical production is the primary source of this acetaldehyde, its presence over oceans is due to the creation of acetaldehyde by photolysis of VOC outflows, but this suggestion has yet to be verified.

Acetaldehyde has been studied extensively in the infrared spectral region, particularly in the comprehensive work of Hollenstein and Günthard [10], in which five isotopic species were analyzed at medium spectral resolution ($\geq 0.4 \text{ cm}^{-1}$) in both the solid state and gas phase from 400–4000 cm^{-1} .

When it was first identified that acetaldehyde is an important trace species in atmospheric chemistry acting as a precursor to the formation of many VOCs in the free troposphere and a known lachrymator in photochemical smog, efforts were made to measure absolute infrared intensity values in the gas-phase in order to quantitatively measure atmospheric concentrations [11].

Since then, further efforts have been made to complete the initial work of Hollenstein and Günthard by using much higher spectral resolution. Kleiner [12–14] worked extensively with acetaldehyde by recording and assigning spectra of the fundamental torsion band (ν_{15}) observed around 150 cm^{-1} , the C–C–H bending fundamental (ν_{14}) centered at 764 cm^{-1} , and the ν_5 and ν_{12} methyl C–H modes at 1430 cm^{-1} using a FTS equipped either with a long multipass cell or with a multinozzle long absorption path supersonic expansion. This was complemented by the investigation of Andrews [15], who assigned spectra of the ν_9 C–C stretching fundamental at 867 cm^{-1} recorded using a diode laser with a slit-jet nozzle expansion and in a room-temperature gas cell using an FTS.

There are two bands of acetaldehyde, which are of particular interest as possible candidates for retrieval with ACE: the ν_3 C–H stretching fundamental at 2715.77 cm^{-1} and the $2\nu_6$ overtone with its Q-branch centered at 2823.30 cm^{-1} [16]. Both bands are located in regions of the atmospheric spectrum that are relatively free of interfering species which may have rovibrational lines that overlap with those of acetaldehyde, thus inhibiting its retrieval. Retrievals of concentration profiles from satellite data require accurate laboratory spectroscopic measurements in the form of either line parameters [17] or absorption cross-sections [18]. HITRAN is an excellent source of this type of spectroscopic data [19]; however, the database does not currently contain an entry for acetaldehyde so measuring a set of absorption cross-sections was necessary.

In this work, a set of high-resolution infrared spectra of mixtures of acetaldehyde vapor combined with pure

synthetic air have been measured at various temperatures and pressure to simulate atmospheric conditions encountered in the free troposphere and lower stratosphere. The band intensities were calibrated using acetaldehyde spectra provided by the Pacific Northwest National Laboratory (PNNL) IR database [20]. This work is similar to previous measurements of the 3 μm infrared absorption cross-sections of ethane [21].

2. Experimental

2.1. Spectrometer

All absorption spectra were recorded at the University of York using a high-resolution FTIR spectrometer (Bruker IFS 125/HR) with a CaF_2 beamsplitter, LN_2 -cooled indium antimonide (InSb) detector and the internal mid-IR radiation source (globar). A 3 μm red pass optical filter was employed to restrict the spectral sampling of the spectrometer to the region between 1800 and 3500 cm^{-1} .

2.2. Gas cell

A 20-cm long single-pass, stainless steel absorption cell was used for all measurements. The design is that of a double-walled cylinder with CaF_2 windows sealed using o-rings made of a red iron oxide filled, Phenyl/Methyl Silicone Rubber, 68°IRHD that has a minimum working temperature < –100 °C and remains flexible, serving to minimize leak problems at low temperatures.

The cell was mounted inside one of the two absorption sample chambers of the spectrometer and evacuated to a pressure of < 5.0 Pa to reduce the problem of interfering gaseous impurities, primarily H_2O and CO_2 . Cell temperatures below the ambient room temperature were attained by circulating Syltherm Silicone Thermal Fluid XLT (Dow Chemical), refrigerated by a NESLAB ULT-80 low temperature bath circulator, through cooling coils wrapped around the outer wall of the inner cylinder of the gas chamber. Temperature was recorded using the readout of the circulation unit and confirmed by using a low-temperature alcohol thermometer placed in the refrigerant reservoir.

2.3. Preparation of sample

Acetaldehyde of $\geq 99.5\%$ purity was supplied by Sigma-Aldrich. Synthetic air was provided by Air Products in the form of Air Zero Plus (20.9% $\text{O}_2 \pm 0.2\%$, $\text{H}_2\text{O} \leq 0.5$ ppm, $\text{CH}_4 \leq 0.05$ ppm, $\text{CO} + \text{CO}_2 \leq 0.1$ ppm, 99.99990% overall purity). Measurements were carried out by mixing (approx. 10 Torr) the acetaldehyde vapor with dry synthetic air in order to simulate atmospheric pressure-broadened spectra, the mixing ratios were chosen such that self-broadening of rovibrational lines can be neglected.

Gas mixing and pressure measurements were performed in 0.5 in. diameter gas lines that attached directly to the gas cell. The mixture was produced by introducing a small amount of acetaldehyde vapor directly into the cell from a sealed glass sample tube followed by the addition of synthetic air. The pressures were measured

using full scale 10,100 and 1000 Torr Baratron capacitance manometers (MKS).

2.4. Spectral measurements

A summary of the pressures, temperatures and instrument parameters for all measurements are detailed in Table 1. Spectra were measured at a resolution of 0.005 cm^{-1} (calculated as 0.9/MOPD using the Bruker definition of resolution) using the Norton–Beer weak apodization function and were the accumulated average of 200 scans, which took approximately 2.5 h to record. Background spectra were recorded before (200 scans) and after (200 scans) the sample measurement. These measurements were performed with the cell containing only synthetic air with a total pressure equivalent to the combined pressure of analyte vapor and synthetic air during the sample measurement.

2.5. Errors

Since temperature measurements were conducted by recording the temperature of the refrigerant within the well of the circulation unit, errors in temperature will arise since the load (gas cell) being cooled by the refrigeration unit will have temperatures slightly higher than that of the refrigerant being flowed through it. An error in the measurement can be estimated from the lowest temperature measurements made using the gas cell (200 K) where the maximum attainable pressure of acetaldehyde gas flowed into the cooled, empty cell was approximately 4 Torr before condensing into liquid within the cell. The vapor pressure curve of acetaldehyde indicates that a pressure of 4 Torr corresponds to a temperature of roughly 204 K. This would indicate that for the system, the maximum difference between the measured and actual cell temperature is +4 K, which corresponds to an error of 2.0% at 200 K.

The uncertainties in the pressure readings are estimated to be 0.5%. Due to the method of preparing acetaldehyde/synthetic air mixtures (detailed above), it is expected that there be some residual acetaldehyde vapor forced into the

cell when the synthetic air is added to the cell resulting in higher amounts of acetaldehyde in the cell than indicated by the pressure gauge. Once the cell is filled, it is isolated from the gas line using a shut-off valve that is directly connected to the cell to prevent impurities entering the cell and to ensure a stable temperature during measurement.

The overall uncertainties in the absorption cross-sections reported in this work are estimated to be $\pm 5\%$.

3. Results and discussion

3.1. Data analysis

Transmission spectra for the experiments were calculated by dividing the averaged single-channel sample scans by the associated two background spectra. A routine baseline correction was performed for all of the ratioed spectra such that it extended to 100% transmittance. Calibration of the line positions was performed by multiplying the wavenumber axis of the spectrum with a correction factor that was calculated from pure methane spectra that were recorded in the cell in the same spectral region using the HITRAN database [19].

The relative intensities of the absorption cross-sections measured were calibrated using spectra provided by the Pacific Northwest National Laboratory (PNNL) IR database (<http://nwir.pnl.gov>) [20]. The procedure used to calibrate the spectra begins by converting transmission spectra to PNNL units ($\text{ppm}^{-1}\text{ m}^{-1}$), which is the absorbance for a sample concentration of 1 ppm over an optical path length of 1 m at a temperature of 296 K, using the equation:

$$\varepsilon_{\text{PNNL}}(\nu, T) = -\frac{T}{296} \frac{0.101325}{Pl} \log_{10} \tau(\nu, T)$$

where $\tau(\nu, T)$ is the transmittance at wavenumber ν (cm^{-1}) and temperature T (K), P is the pressure of the absorbing gas (Pa), and l is the path length (m). Transmission intensities were integrated between 2400–3400 cm^{-1} . The PNNL database contains three spectra of acetaldehyde measured at 278, 298 and 323 K. These were integrated over the same spectral range and the same area under the curve was obtained to within 0.5%. All $\varepsilon_{\text{PNNL}}(\nu, T)$ were calibrated by normalizing with the average area from the three spectra of acetaldehyde in the PNNL database. It was found that our $\varepsilon_{\text{PNNL}}(\nu, T)$ values needed to be reduced by about 2.3% to be in agreement with the PNNL data.

Spectral absorption cross-sections, $\sigma(\nu, T)$ in units of $\text{cm}^2\text{ molecule}^{-1}$, were calculated using the equation [21]:

$$\sigma(\nu, T) = -\xi \frac{10^4 k_B T \ln \tau(\nu, T)}{Pl}$$

where k_B is the Boltzmann constant and ξ is the scaling factor needed to convert the relative intensities of each spectrum to their equivalent PNNL values. Figs. 1 and 2 show examples of the recorded cross-sections of acetaldehyde; the first figure provides an overview of the entire 3 μm region, while the second provides a close-up of the pressure-temperature dependence of individual spectral features. Spectral absorption cross-sections corresponding to the experimental conditions outlined in Table 1 are available electronically upon request from the authors.

Table 1

Summary of the pressure and temperature parameters.

Acetaldehyde pressure (Torr)	Total pressure (Torr)	Temperature (K)
10.05	762.23	297
10.03	605.41	297
10.07	375.00	296
10.03	602.25	270
10.25	451.21	270
10.07	302.18	270
10.11	601.58	250
10.02	402.61	250
9.98	200.21	250
10.30	300.40	215
10.04	200.13	215
10.32	102.40	215
10.07	50.21	215
3.92	102.00	200
3.96	75.30	200
4.04	50.90	200

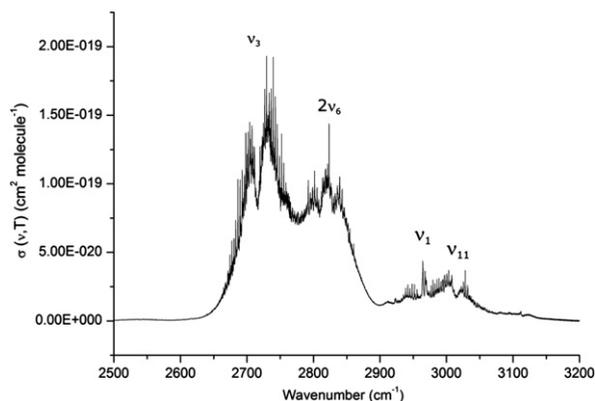


Fig. 1. Absorption cross-sections in the 3 μm region of acetaldehyde at 250 K.

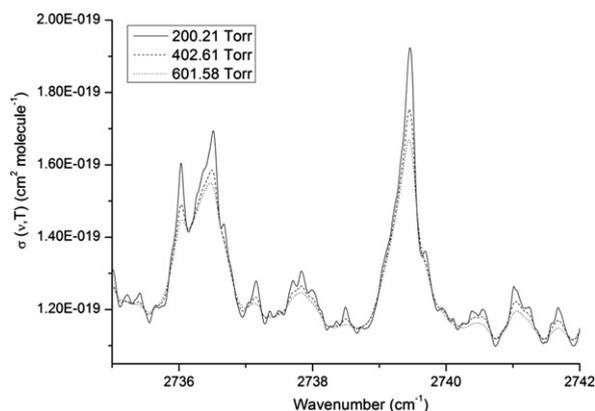


Fig. 2. Absorption cross-sections illustrating the pressure dependence of lines in the R-branch of the ν_3 band of acetaldehyde at 250 K.

4. Conclusions

Infrared absorption cross-sections for acetaldehyde have been measured in the 3 μm region ($2400\text{--}3400\text{ cm}^{-1}$) from spectra obtained using a FTIR spectrometer at a resolution of 0.005 cm^{-1} . The data was recorded for mixtures of acetaldehyde vapor combined with pure synthetic air taken with a range of temperatures and pressures to simulate the atmospheric conditions found in the Earth's troposphere and lower stratosphere. Relative intensities were calibrated using three acetaldehyde spectra obtained from the PNNL IR database. These cross-sections will be utilized to retrieve acetaldehyde from orbit with the ACE-FTS.

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