



Infrared absorption cross sections for acetone (propanone) in the 3 μm region

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ABSTRACT

Infrared absorption cross sections for acetone (propanone), $\text{CH}_3\text{C}(\text{O})\text{CH}_3$, have been determined in the 3 μm spectral region from spectra recorded using a high-resolution FTIR spectrometer (Bruker IFS 125 HR) and a multipass cell with a maximum optical path length of 19.3 m. The spectra of mixtures of acetone with dry synthetic air were recorded at 0.015 cm^{-1} resolution (calculated as 0.9/MOPD using the Bruker definition of resolution) at a number of temperatures and pressures (50–760 Torr and 195–296 K) appropriate for atmospheric conditions. Intensities were calibrated using three acetone spectra (recorded at 278, 293 and 323 K) taken from the Pacific Northwest National Laboratory (PNNL) IR database.

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1. Introduction

Acetone (propanone), $\text{CH}_3\text{C}(\text{O})\text{CH}_3$, was first obtained from the destructive distillation of acetates and acetic acid, but it was not until 1832 that its molecular formula was correctly determined [1]. It is widely used as an organic solvent in lacquers, varnishes, pharmaceuticals, and cosmetics, and in numerous applications in the chemical industry as a chemical feedstock and intermediate.

Important uses are in the production of methyl methacrylate (MMA) and bisphenol A (BPA) [1]. MMA is polymerised to produce plexiglas (perspex), used principally as a substitute for glass, which is also incorporated into paints, lacquers, enamels, and coatings. BPA is used primarily to make polycarbonate plastics, which are tough and durable and commonly found in everyday items such as water bottles, food containers, bicycle helmets, compact discs, digital versatile discs, and monocle lenses.

Acetone is not only important to our modern way of life, but also to the chemistry of the atmosphere. Background mixing ratios in the free troposphere range from about 500 pptv at northern mid-latitudes to about 200 pptv at southern latitudes [2]. Mixing ratios exceeding 2 ppbv in the free troposphere have also been observed, for example in biomass burning plumes [3].

Acetone has only a negligible direct radiative forcing effect; however, like many volatile organic compounds (VOCs) it has a significant impact on air quality and is implicated in the production of tropospheric ozone, which is toxic and a strong greenhouse gas. The 2007 IPCC report [4] lists tropospheric ozone as the third most important anthropogenic factor (after methane and carbon dioxide) in driving climate change.

There is considerable uncertainty in the processes that control the atmospheric abundance of acetone. Sources of acetone include plant growth, decaying plant matter, atmospheric oxidation of organic compounds such as propane or terpenes, biomass burning, and a small contribution from anthropogenic emissions.

Recently, there has also been uncertainty in the role the oceans play in the acetone budget. Jacobs et al. [5]

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suggest that the oceans contribute about 28% of the atmospheric acetone from microbial and photochemical activity. Their main argument for this is the high acetone concentrations of nearly 400 ppt found in regions of the Pacific Ocean far from any terrestrial sources [6]. However, recent direct measurements of the acetone flux over the oceans have contradicted this conclusion [7], indicating that overall oceans are a large sink for acetone. An extensive global set of acetone profiles would clearly improve and constrain the acetone budget.

The sinks of acetone are primarily photolysis and reaction with OH, with a minor contribution from dry deposition. Photolytic dissociation to form the acetyl (CH_3CO) and methyl (CH_3) radicals accounts for about 50% of this, ensuring that acetone is a key part of chemistry in the atmosphere. Reactions of the acetyl radical in the upper troposphere are a major source of HO_x ($\text{OH}+\text{HO}_2$) radicals and peroxyacetyl nitrate (PAN). PAN acts as a major NO_x ($\text{NO}+\text{NO}_2$) reservoir in the free troposphere [8]. The lifetime of PAN in the troposphere increases with altitude, due to its greater thermal stability at lower temperatures, increasing from a few hours at the Earth's surface to several months at the tropopause. The relatively long lifetime in the middle and upper troposphere allows it to be transported over long distances, translating to a long-distance transport of NO_x . Nearly all tropospheric ozone results from the photolysis of NO_2 , so for this reason the sources of pollutant emission may in fact be long distances from the regions of resulting elevated ozone [9].

Despite a number of ground-based [10] and airborne measurements [2,6], so far there have been no global measurements of acetone. Increasingly satellite instruments are able to directly observe VOCs, including acetone, in the atmosphere. In particular, the Atmospheric Chemistry Experiment (ACE), on board SCISAT-1, is able to detect more organic molecules in the troposphere than any other satellite instrument. In fact, the first detection of acetone using satellite infrared occultation spectroscopy was made by the ACE-FTS instrument, which sampled a biomass burning plume near the east coast of Tanzania on 8 October 2005 [3]. ACE uses a high-resolution Fourier transform spectrometer that covers the spectral region from 750 to 4400 cm^{-1} [11]. Due to this extended spectral coverage, it is possible to carry out retrievals in the strong 3 μm region, where all aliphatic hydrocarbons have their strongest-intensity modes (C–H stretch) and where there are relatively few spectral interferers. This work provides accurate spectroscopic measurements that will enable the retrieval of acetone abundances from atmospheric limb spectra recorded by ACE.

Retrievals of concentration profiles from satellite data require accurate laboratory spectroscopic measurements in the form of either line parameters or absorption cross sections. The HITRAN database [12] is a good source of such spectroscopic data; however, it does not contain acetone. Acetone data are also contained in the Pacific Northwest National Laboratory (PNNL) IR database (<http://nwir.pnl.gov>) [13]; however, these are not suitable for remote sensing of the upper troposphere for a number of reasons. All PNNL spectra are recorded at relatively low resolution (0.112 cm^{-1}) as mixtures with pure

nitrogen gas, not synthetic air, at pressures of 760 Torr and temperatures of 278, 293, or 323 K. Despite not being suitable, these data have previously been used to retrieve acetone from ACE spectra; in particular using a micro-window centred on the prominent Q branch at 1365.5 cm^{-1} (C–H bending mode) [3].

The sparsity of good spectroscopic acetone data for remote sensing purposes can be explained by the experimental difficulties involved in taking the measurements. Acetone has a low vapour pressure (~ 1 Torr at 213 K and ~ 0.2 Torr at 197 K) [14], meaning that long optical pathlengths must be used for spectroscopic measurements in order to achieve sufficient signal to noise ratios. Until now the only available air-broadened acetone measurements suitable for remote sensing of the upper troposphere were taken by Waterfall in the 700–1780 cm^{-1} spectral region at 0.03 cm^{-1} resolution for the temperatures 224, 233, 253, 272 and 297 K [15]. The spectroscopy in this region has recently been improved and extended to lower temperatures. This will be presented in a future paper.

We have recently determined infrared absorption cross sections in the 3 μm region for air-broadened ethane [16] and propane [17]. In a similar manner, this paper presents a set of infrared absorption cross sections for air-broadened acetone between 2615 and 3300 cm^{-1} , derived from high-resolution (0.015 cm^{-1}) spectra of acetone/synthetic air recorded over a range of pressures and temperatures (50–760 Torr and 195–296 K) appropriate for atmospheric retrievals. Absorption cross sections in this less-congested spectral region will allow ACE acetone retrievals to extend to lower in the troposphere than retrievals using the Q branch at 1365.5 cm^{-1} .

2. Experimental

Experiments were performed at the Molecular Spectroscopy Facility (MSF) located at the Rutherford Appleton Laboratory, Oxfordshire, UK. The measured air-broadened acetone absorption spectra were recorded using a Bruker Optics IFS 125HR high-resolution Fourier transform spectrometer (FTS) with a calcium fluoride beam splitter, indium antimonide (InSb) detector, and an internal mid-infrared radiation source (globar). An optical filter restricted the throughput to the spectral region 2400–3500 cm^{-1} , thus reducing photon noise. The aperture diameter (2.5 mm) of the spectrometer was set so that the intensity of infrared radiation falling on the InSb detector was maximised without saturation or loss of spectral resolution. The spectrometer was set to a resolution of 0.015 cm^{-1} (calculated as 0.9/MOPD using the Bruker definition of resolution). Norton–Beer weak apodisation and Mertz phase corrections were applied to all interferograms. The FTS was evacuated to a pressure below 0.2 Pa by a turbo-molecular pump to minimise the absorbance of impurity atmospheric gases in the optical path. The FTS instrumental parameters and settings are summarised in Table 1.

The MSF short-path absorption cell (SPAC) [18] was used for all measurements. The SPAC is a multipass cell with mirrors at each end to reflect the radiation back and

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