



## Infrared absorption cross sections for methanol

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### ABSTRACT

Infrared absorption cross sections for methanol, CH<sub>3</sub>OH, have been determined near 3.4 and 10 μm from spectra recorded using a high-resolution FTIR spectrometer (Bruker IFS 125HR) and a multipass cell with a maximum optical path length of 19.3 m. Methanol/dry synthetic air mixtures were prepared and spectra were recorded at 0.015 cm<sup>-1</sup> resolution (calculated as 0.9/MOPD) at a number of temperatures and pressures (50–760 Torr and 204–296 K) appropriate for atmospheric conditions. Intensities were calibrated using composite methanol spectra taken from the Pacific Northwest National Laboratory (PNNL) IR database. The new measurements in the 10 μm region indicate problems with the existing methanol spectroscopic line parameters in the HITRAN database, which will impact the accuracy of satellite retrievals.

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### 1. Introduction

Methanol, the simplest of the organic alcohols, was first isolated in 1661 by Robert Boyle from the destructive distillation of boxwood [1]. Whereas the two-carbon analogue, ethanol, is a popular recreational drug, methanol is highly toxic to humans, causing blindness and/or death. Methanol is one of the main chemical commodities traded around the world, and is produced on an industrial scale, starting from synthesis gas, a mixture of CO and H<sub>2</sub>, formed from the reaction of natural gas (principally CH<sub>4</sub>) with steam or O<sub>2</sub>. At high pressures, methanol is formed by the reaction of CO and H<sub>2</sub> over a catalyst (Cu and Zn/Mn/Al oxides).

Methanol is a common organic solvent, and is finding growing use [2] as a transportation fuel, a fuel additive, a hydrogen carrier in fuel cells, and in various processes

such as biodiesel transesterification and wastewater denitrification. Its main use, however, is as a feedstock in the manufacture of other chemicals, including formaldehyde, (~ 40% of methanol supplies) and acetic acid. It also has important uses in the production of methyl methacrylate (MMA) and dimethyl terephthalate (DMT), both esters of methanol [1]. MMA is used in the manufacture of poly(methyl methacrylate) (PMMA), also known as Plexiglas or Perspex, used principally as a substitute for glass and also incorporated into paints, lacquers, enamels, and coatings. DMT is used in the manufacture of polyesters and plastics, e.g. polyethylene terephthalate (PET), used extensively in making plastic containers.

Methanol is not only important to our modern way of life, but also to interstellar chemistry because its formation provides a pathway to more complex organic molecules that are necessary for life. In the interstellar medium, methanol forms predominantly by successive hydrogenation of solid CO on the surfaces of dust grains [3]. Interstellar methanol was first discovered by Ball et al. in 1970 [4] in radio emission toward the galactic centre, and has since been detected in cometary atmospheres [5,6]. Empirical line intensities of methanol in the 300–500 cm<sup>-1</sup> region

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have recently been obtained to support astronomical observations taken from orbit by the Heterodyne Instrument for Far Infrared (HIFI) instrument on the Herschel Space Observatory [7].

Closer to home, methanol is the second most abundant organic molecule in the Earth's atmosphere after methane [8], and its primary emissions contribute approximately 6% of the total terrestrial biogenic emissions of organic carbon [9]. According to Jacobs et al. [10], methanol emissions amount to 206 Tg yr<sup>-1</sup>, arising from plant growth (62%), plant decay (11%), atmospheric oxidation of methane and other hydrocarbons (18%), biomass burning and biofuels (6%), and vehicles and industrial activities (2%).

The background concentration of methanol in the free troposphere ranges from ~0.4 to ~0.7 parts per billion (ppb) [11]. The main sink mechanism for methanol is oxidation by the OH radical to produce formaldehyde, HCHO. The effectiveness of this reaction is the primary reason for methanol's short lifetime, which is about one week [10].

Methanol has a negligible direct radiative forcing effect due to its short atmospheric lifetime. 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 [12] lists tropospheric ozone as the third most important anthropogenic factor (after methane and carbon dioxide) in driving climate change. In the troposphere, methanol reacts with the OH radical, thereby lowering the amount of OH available to react with strong greenhouse gases such as CH<sub>4</sub>; the result of this is to lengthen the CH<sub>4</sub> lifetime. Methanol, therefore, has an indirect contribution to radiative forcing; the 2007 IPCC report gives a calculated value of 2.8 for the indirect 100-year GWP (see Table 2.15 in Ref. [11]).

Increasingly satellite instruments are able to directly observe VOCs in the atmosphere. In particular, the Atmospheric Chemistry Experiment (ACE), on board SCISAT-1, currently detects more organic molecules than any other satellite instrument. The principal ACE instrument is a high-resolution Fourier transform spectrometer that covers the spectral region from 750 to 4400 cm<sup>-1</sup> [13]. The ACE-FTS detected the first near global distribution of methanol in the upper troposphere (March 2004 to August 2005) [14]. Volume mixing ratios (VMRs) are typically about 0.5 ppb, but can be as high as 4.0 ppb in biomass burning plumes [15]. More recently the Tropospheric Emission Spectrometer (TES) [16] and the Infrared Atmospheric Sounding Interferometer (IASI) [17] have been able to detect enhanced methanol in the thermal infrared by nadir sounding [18]. TES and IASI offer superb global coverage (night and day) compared to ACE, but ACE has the advantage of providing vertical information.

Retrieving the concentrations of atmospheric species from satellite spectra require accurate laboratory spectroscopic measurements in the form of either line parameters or absorption cross sections. Currently v3.0 ACE methanol retrievals cover 5–25 km in altitude and make use of the spectroscopic line parameters in the HITRAN database [19], as derived by Xu et al. [20] in the 10 μm region; this band system is principally associated with the strong fundamental

v<sub>8</sub> mode at 1033 cm<sup>-1</sup> (CO stretch) [21]. The 10 μm region of an ACE spectrum is dominated by saturated ozone lines, which limit the position of the principal retrieval microwindow to the region between 984.9 and 1005.1 cm<sup>-1</sup>, at the edge of the band. On the other hand, retrieval microwindows for the nadir-viewing TES and IASI instruments cover the strong Q branch near 1033 cm<sup>-1</sup>.

For the majority of the methanol 10 μm line parameters in HITRAN, the estimated line intensity uncertainties are in the range ≥ 10% and < 20%. The air-broadened ( $\gamma_{\text{air}}$ ) and self-broadened ( $\gamma_{\text{self}}$ ) half-widths were given assumed values of 0.1 and 0.4 cm<sup>-1</sup> atm<sup>-1</sup>, respectively, with the air-broadened pressure shift ( $\delta_{\text{air}}$ ) given a value of zero. Since the line parameters were derived from a set of room-temperature spectra, the coefficient ( $n_{\text{air}}$ ) for the temperature dependence of  $\gamma_{\text{air}}$  was given an assumed value of 0.75. As these last four parameters have assumed values, HITRAN provides no indication of their errors. Uncertainties in all the spectroscopic line parameters [22], not just the line intensity, contribute to errors in the ACE methanol retrieval, but there is no simple way of knowing how  $\gamma_{\text{air}}$ ,  $\gamma_{\text{self}}$ ,  $n_{\text{air}}$ , and  $\delta_{\text{air}}$  contribute to this overall error without performing laboratory measurements of the 10 μm band system at low temperature.

Typical errors in the ACE methanol VMRs are ~20–30% [14]. In order to improve the accuracy of ACE retrievals, new spectroscopic data for the methanol band near 3.4 μm, which lies in a less-congested region of the spectrum, have been obtained in the form of absorption cross sections over a range of pressures and temperatures (50–760 Torr and 204–296 K). Currently the HITRAN database contains no data in this spectral region, largely because of the difficulties in making unambiguous assignments for individual lines; the most intense spectral lines in this region are densely packed into an interval of ~500 cm<sup>-1</sup>. This band system is associated with three CH stretch fundamental modes, v<sub>3</sub> at 2844 cm<sup>-1</sup> (symmetric), v<sub>2</sub> at 3000 cm<sup>-1</sup> and v<sub>9</sub> at 2960 cm<sup>-1</sup> (both asymmetric). There have been a number of efforts to model and quantify the CH stretch region of methanol [23–25]; most recently, a new line-by-line model for the v<sub>3</sub> band has been constructed [26].

Ideally, in the future ACE retrievals will make use of both absorption bands at 3.4 and 10 μm, so it is crucial that the intensities for these two regions are consistent. Additional measurements have been made in the 10 μm region over a range of pressures and temperatures (50–760 Torr and 204–296 K) to compare with the existing HITRAN data. This work provides the first low temperature quantitative measurements of methanol for atmospheric remote-sensing purposes. Such measurements are difficult because methanol has a low vapour pressure at low temperatures (~1.0 Torr at 230 K and ~0.05 Torr at 203 K) [27], so that long optical pathlengths must be used for spectroscopic measurements in order to achieve sufficient signal-to-noise ratios.

## 2. Air-broadened spectral measurements of methanol

Air-broadened methanol absorption spectra were recorded at the Molecular Spectroscopy Facility (MSF), Rutherford Appleton Laboratory (located in Oxfordshire,

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